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CARBON ISOTOPES IN OIL-GAS GEOLOGY

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E. M. Galimov E. M.

"Nedra" Press,
Moscow, 1973

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16. Abstract

Analysis of variations in the natural abundances of the carbon isotopes C^{12} and C^{13} in petroleum, gases, bitumens, and other materials is treated in this monograph. A theoretical-calculation division of the book gives new data on the thermodynamic isotope effects of organic compounds; this division also presents, for the first time, a theory of biogenic isotope equilibria and intramolecular isotope nonuniformity of bio-organic compounds. Laboratory studies of processes simulating natural fractionation of carbon isotopes are emphasized. Included in the monograph are data on the isotopic composition of individual hydrocarbons. Possible pathways of their formation are examined and a general model of the petroleum-forming process is proposed. Within the bounds of a specific region, genetical types of petroleum are found and their areal and profile distributions are established.

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AUTHOR'S ABSTRACT /2

Galimov, E. M. Izotopy ugleroda v neftegazovoy geologii /Carbon Isotopes in Oil-Gas Geology/, Moscow, "Nedra", 1973, 384 pp.

The monograph is devoted to problems of organic chemistry and oil-gas geology through a study of variations in the natural abundances of carbon isotopes C^{12} and C^{13} in petroleum, gases, bitumens, and other materials.

The book contains a calculation-theoretical part in which are given new data on the thermodynamic isotope effects of organic compounds and which present for the first time a theory of biogenic isotope equilibria and intramolecular isotope nonuniformity of bio-organic compounds. Much attention is given to the results of a laboratory study of processes simulating natural fractionation of carbon isotopes.

Included are data on the isotopic composition of individual hydrocarbons, various structural groups of hydrocarbons of petroleum and of nonhydrocarbon constituents. Possible pathways of their formation are examined and a general model of the petroleum-forming process is proposed. Within the limits of a specific region, genetic types of petroleum are found and the limits of their distribution along the profile and areally are established. Methods of determining, from the results of integrated chemical and isotopic analysis of gas composition, the features of their origin and the migratory processes that have occurred are outlined, along with a reconstruction of the general pattern of the formation of gas deposits within the limits of the region investigated. Experimental data are given on the isotopic composition of the carbon in bitumens, gases, graphites, and other carbonaceous formations of metamorphic, hydrothermal, and igneous rocks. The mechanism of carbon isotope fractionation in the endogenic is examined and distinguishing features of carbon compounds formed biogenically and abiogenically are established.

The book is intended for geologists, but its theoretical part is of interest to biochemists and specialists in the chemistry of stable isotopes.

Tables: 84, illustrations: 101, and bibliographic references: 235.

FOREWORD /3

The application in geology of isotopy of stable nuclei and variations in the natural abundances of isotopes finds expression in two interrelated, but essentially different methods.

The first method is based on the proximity of the properties of isotopes and stability owing to this isotopic composition of an element in physicochemical processes; through this proximity one can establish the origin of a compound studied, although between it and the original compound there may lie a long chain of chemical transformations. Essentially, this is the method of natural labeled atoms, particularly effective when solving genetical problems.

But much more in the spirit of isotope geochemistry is another method, which utilizes the nonidentity of the properties of isotopes and which permits the study of geochemical processes from the results of the fractionation of isotopes in physicochemical systems. Essentially, this method amounts to comparing the observed (measured) distribution of isotopes in natural constituents of a system under study with partition coefficients established theoretically (by the methods of quantum chemistry) or experimentally for a given system under specified conditions. It is precisely this second approach that is dominant in this book.

Ordinarily, isotope geochemistry deals with two main types /4
of isotope effects -- thermodynamic and kinetic. It is held (and the author shares this point of view) that in isotopes in which complex organic compounds participate, isotope fractionation is determined chiefly by the kinetic isotope effects. Thermodynamic isotope effects characterize isotope fractionation in isotope exchange equilibria, characteristic of primitive systems of the type CO_2 -- $CO_3^=$ or CO_2 -- CH_4, but as it is believed, are not realized in systems containing polyatomic organic compounds, in particular, in biological systems. Experimental studies show that the rate of carbon isotope exchange between organic compounds,

including between hydrocarbons, is actually low. But this pertains to nonliving systems. In biological systems, as it was unexpectedly found, an exceptionally large role is that of thermodynamic isotopic effects. This makes it possible in many cases to look at entirely differently the causes of the fractionation of isotopes in the conversion of organic matter and therefore in processes of petroleum and gas formation and accounts for the place given in this book to problems of isotopic thermodynamics.

To understand these new concepts, obviously it is appropriate to say something about the basis from which they sprang.

In 1967, in our laboratory (Mass Spectrometry Laboratory in the Moscow Institute of the Petrochemical and Gas Industry imeni I. M. Gubkin), at the same time that experimental work on the isotopic composition of natural hydrocarbons was begun, the first attempts were made to calculate thermodynamic isotopic factors (β-factors) of hydrocarbons. The computational part of the work was done by A. A. Ivlev. Earlier, study of isotopic equilibria of carbon was limited primarily to compounds containing one exchangeable item each: CO, CO_2, $CO_3^=$, HCN, and so on. The values determining the behavior of these compounds in isotope exchange reactions (ratios of the statistical sums) were obtained by H. C. Urey. A series of constants was calculated by H. Craig, Y. Bottinga, and H. Johansen. However, there are no data for more complicated compounds, including hydrocarbons. We began this work with a limited aim -- to determine the theoretically possible magnitude and temperature dependence of thermodynamic isotopic effects in hydrocarbons and to attempt to estimate on this basis the temperature limits of the petroleum-forming process. It should be noted that the results of the first calculations were inexact. In particular, in subsequent calculations a temperature inversion in the system CH_4 -- C_2H_6 -- C_3H_8 which was indicated earlier /4/ failed to be confirmed. Incidentally, this does not involve the essentials of the then-reached conclusion on low-temperature conditions of petroleum formation. Later, in collaboration with professor L. A. Gribov, a program for calculating thermodynamic /5 isotope factors utilizing a program for calculating vibrational frequencies of polyatomic compounds developed earlier by L. A. Gribov and coworkers, was formulated. Based on this program, thermodynamic isotopic factors of paraffinic (normal alkanes), naphthenic (cyclohexane), aromatic (benzene and toluene) hydrocarbons, and several heteroatomic organic compounds were calculated.

All these compounds contain several carbon atoms. Since carbon atoms in a polyatomic compound occupy nonequivalent (in respect to symmetry operations) positions and enter into different bond types, the question was raised as to how this can be taken into account in representing the β-factor. An essential general expression for the β-factor was derived. It was found that

besides the thermodynamic isotopic factor characterizing a compound overall (which was called the β_{Σ}-factor), physically meaningful is a certain quantity characterizing isotope exchange properties of the atom in the given structural position (β_i-factor). This led to the concept of intramolecular thermodynamic isotope effects.

A turning point in the author's concept of the role of thermodynamic isotope effects in processes associated with the biological cycle was the discovery of a phenomenon, now called the biogenic isotopic equilibrium of carbon. First, it was possible to establish that thermodynamic isotopic factors can be calculated to a good approximation by using several quantities that characterize -- at a given temperature -- a specific type of chemical bonding in the compound. Through this, the complicated problem of calculating β-factors, requiring large outlays of highly qualified labor in preparing the initial information and large investments of machine time to find the optimal solution variant, was reduced to the nearly implausibly simple operation of adding several numbers (the isotopic bond numbers), determined by the nature of the chemical bonds in the molecule under investigation. This not only did away with the necessity of laborious calculations of the β-factors in terms of the vibrational frequencies of isotopic species but also made it possible to determine the β-factors of such complicated organic compounds whose calculation by the direct method is virtually unattainable.

By arriving at this method, it was not difficult to calculate β-factors of many new organic compounds. This was done, in particular, for compounds that are the main structural forms and the main types of biochemical constituents of organic matter. A comparison of these results with available data on the isotopic composition of these constituents showed that compounds characterized by the largest β-factors correspond to the constituents of organic matter which to the greatest extent are enriched with /6 the C^{13} isotope. This correspondence, characteristic of all the compounds investigated, indicated the existence of a special mechanism responsible for the distribution of carbon isotopes in the biochemical constituents of organisms or in compounds traversing the biological cycle, in accordance with their thermodynamic isotopic factors. Hence was formulated the conclusion that there exists an isotope exchange equilibrium of carbon in biological systems and that the isotope effect of photosynthesis is predominantly isotope-exchange in character, where previously the isotope effect of photosynthesis had been accounted for exclusively by kinetic factors.

The extention of the concept of biogenic equilibria to intramolecular thermodynamic isotope effects led to the conclusion that biogenic intramolecular isotopic nonuniformity exists. Based

on this conclusion, it was found possible to explain and describe the dependence of the isotopic composition of gases on the degree of metamorphism of the organic compound, and even on the temperature of the basin in which the initial organic compound was deposited, the dependence of the isotopic composition of petroleum hydrocarbons on their structure (degree of branching and cyclicity), and to formulate a criterion for distinguishing between biogenic and abiogenic organic compounds. To put it briefly, on this basis, as the reader will see, one can account for a certain set of facts dealing with the distribution of carbon isotopes in petroleum and gases, and also outline the main ways of utilizing the isotopic analysis of hydrocarbons for their genetic identification, elucidation of migratory processes, evaluating the formation of deposits, and so on.

Thus, the concept of the existence of thermodynamic isotopic effects of this special kind (biogenic isotopic equilibria of carbon and intramolecular isotopic nonuniformity of biogenic organic compounds) determined the heart of the approach which in this book is used most often in interpreting data. The data themselves are partially the results of experiments on the separation of carbon isotopes in processes simulating possible natural mechanisms of isotope fractionation, for example, thermocatalytic synthesis of hydrocarbons from oleic acid, mild pyrolysis of petroleum and natural gas, Rayleigh depletion, dissolution, degassing, and so on. But for the most part, this is data on the isotopic composition of carbon in petroleum, gases, bitumens, and organic matter from various deposits -- totaling more than 2000 determinations. Most of them were obtained under the program "Study of Isotopic Composition of Carbon in Petroleum and Gases of the Perm Ural Area," financed by the Permneft' Association (chief geologist S. A. Vinnikovskiy) since 1967.

It should be noted that even petroleum deriving from oil-bearing provinces widely separated from each other and lying in beds of different geological ages and lithogo-facies composition are quite similar in carbon isotopic composition. This hampers the application of isotope data in solving particular problems of the geology of petroleum within a specific region, since the corresponding variations in isotopic composition are extremely small. In these conditions, added importance lies in a high precision of analysis, and no less so, in an objective estimation of the errors of measurement, making it possible to determine the confidence level of the results and their geochemical interpretation. /7

Though the method and equipment used in mass-spectrometric measurements are not examined in this monograph, in the practical activity of the laboratory these questions were given a great deal of attention. Besides improvements made in the measuring

equipment and in the techniques of preparing the samples for analysis, methods of introducing several correcting factors were developed, allowing for the effect of background, deviation of the measurement regime from the compensation regime, discriminating properties of the admission and analytical channels of the mass spectrometer, and so on. Use was made of a system of interlinked intermediate standards with good tie-in to the familiar PDB standard. Thus, it was found possible to have the error of a series analysis not exceed $\pm$ 0.04 percent, taking the tie-in to the PDB standard into account. All the δC^{13} values in this study were given with respect to the PDB standard. We recall that $\delta C^{13} = \left(\overline{C}^{13}/C^{12}\right)_{sam}/(C^{13}/C^{12})_{PDB}$ -- 1/·100 percent, where $(C^{13}/C^{12})_{PDB} = 0.0112372$. This error ($\pm$ 0.04 percent) is reached at a confidence level of 0.95, that is, it serves as a mathematical expression of the guarantee that in 95 cases out of 100 the measurement error does not go beyond these limits. The actual reproducibility of the results usually lies within the limits $\pm$ ().01-0.02) percent. [PDB = Peedee formation belemnites, South Carolina]

The precision reached makes it possible to confidently distinguish by isotopic composition individual hydrocarbons, structural groups and fractions in the composition of the same petroleum stock, where the difference in the relative content of carbon isotopes is in the hundredths of a percent. In spite of the fact that the range of the fluctuations in isotopic composition of the petroleum stock investigated from the deposits of the Permian Ural Area is only 0.4 percent, in this range it was possible to establish the presence of petroleum of different genetic types, to discover their location areawise, and to find certain correlations in the distribution of carbon isotopes in petroleum hydrocarbons that indicate the character of petroleum-forming processes.

Upon studying the isotopic composition of carbon and petroleum, the aim was to explore in as great detail as possible the isotopic composition of particular classes of hydrocarbons and narrow petroleum fractions, and specific hydrocarbons. Unfortunately, these investigations were limited by the restricted /8
preparative capabilities. Nonetheless, it was possible to isolate and for the first time determine the isotopic composition individually of isoparaffinic, normal paraffinic, and naphthenic hydrocarbons, and aromatic hydrocarbons of varying cyclicity, as well as to study the distribution of carbon isotopes in methane-naphthenic and aromatic constituents narrow fractions of a series of crude oils.

Correlations in the distribution of isotopes in petroleum hydrocarbons generally reflected in the composite results of

isotopic effects intrinsic to different chemical reactions. In each case the isotopic effect is determined by the composition of the reacting system, and by the reaction conditions and mechanism. Quite obviously, conclusions of a geological kind can be made only from a clear knowledge of the chemistry of the corresponding process, therefore in this monograph much attention is given to the chemical aspects of petroleum formation, discussion of the possible mechanisms for the formation of normal and isoparaffinic hydrocarbons, naphthenic and aromatic structures, cyclization mechanisms, and so on. In particular, the principle of petroleum formation based on the idea of the key role of radical-chain reactions is proposed; this principle can satisfactorily explain several correlations in the distribution of carbon isotopes in hydrocarbon constituents and fractions of crude oil. The general approach that we have tried to follow is above all to construct some idea of the physicochemical factors responsible for the observed isotope distribution, and on the basis of the level of understanding we have achieved, to attempt to interpret available data geologically.

Since some theoretical premises are presented in this study for the first time, willy-nilly we have had to introduce new terms and concepts. Such, for example, is the case for the thermodynamic isotopic factor of a compound -- β_c and the internal thermodynamic isotopic factor -- β_i, the isotopic bond number, the coefficient of intramolecular isotopic nonuniformity, the coefficient of biochemical isotopic equilibrium, and so on. It should also be noted that we express the value of δC^{13} in percentages (%), while some investigators report results of isotopic composition measurements in per mils (0/00). This pertains primarily to studies by foreign authors. Obviously, there is no advantage in convenience in reading values in any particular form (for example, δC^{13} = -2.22 percent, or δC^{13} = -22.2 0/00 /original has % -- translator/). It should not be assumed that in contrast to the foreign scientific-technical literature where scales such as per mils or parts per million (ppm) are widespread, in the domestic only percentages are used as the fraction of decimal scale bearing a special designation, while in the remaining cases multiplication by 10^{-n} is used. Therefore we continue to adhere to the scale of δC^{13} values in percentages established in the /9
first domestic studies on isotope geochemistry. Sometimes data in per mils are introduced with a second significant decimal place, for example, 22.22 0/00, which gives the impression of analytical precision that is 10 times higher. But this is a large exaggeration, at least if one judges from the working materials which the author has been able to see in the various laboratories.

In this book there is no systematic exposition of the chemistry and geochemistry of isotopes. In many cases it was necessary to rely on the previous familiarity of the reader with the main correlations of the geological behavior of carbon isotopes. This purpose can be fulfilled by the author's work, Geokhimiya stabil'nykh izotopov ugleroda /Geochemistry of Stable Carbon Isotopes/, published in 1968. It has become obsolete in many respects, but can prove useful as an introduction.

The author is deeply grateful to Academician A. P. Vinogradov and Corresponding Member of the USSR Academy of Sciences N. B. Vassoyevich for discussion of problems dealt with in the book, and for very useful comments, and to the head of the field geophysics of the Moscow Institute of the Petrochemical and Gas Industry (MINKh and GP) imeni I. M. Gubkin, Professor V. N. Dakhnov, and to the chief geologist of the Permneft' Association, S. A. Vinnikovskiy for their support of work carried out in the Mass Spectrometry Laboratory, to Corresponding Member of the USSR Academy of Sciences A. B. Ronov, professors M. V. Ivanov, I. A. Petersil'ye, V. S. Prokhorov, Ye. N. Ivanov, A. A. Migdisov, A. A. Ivlev, A. Z. Koblova, and I. G. Kalachnikova for participation in combined investigations, whose results are used in the book.

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CARBON ISOTOPES IN OIL-GAS GEOLOGY

E. M. Galimov

CHAPTER ONE

THERMODYNAMICS OF ISOTOPE EXCHANGE

Quantum-Statistical Concepts of Thermodynamic Isotope Effects

If by some method one can calculate the internal energy of system components, then one can find for given conditions all the thermodynamic parameters determining the chemical content of the process: enthalpy $H = U + RT$, entropy $S = \int\left(\frac{\partial U}{\partial T}\right) d \ln T$, isobaric-isothermal potential $Z = H - TS$, heat capacity $c_V = \left(\frac{\partial U}{\partial T}\right)_V$ and $c_P = \left(\frac{\partial U}{\partial T}\right)$ and so on. Here R is the gas constant and T is the absolute temperature. By knowing the Z of the reactants, one can determine its constant from the expression:

$$-\Delta Z = RT \ln K. \qquad \text{(I.1)}$$

Classical thermodynamics gives the relations between the principal thermodynamic parameters, but their quantities are determined by experimental measurements of thermal effects and heat capacities. For the study of isotope effects, this approach would be unpromising in view of the negligible value of the thermal effects of isotopic exchange reactions. Fortunately, quantum mechanics indicates an approach for the direct calculation of the energy of molecules.

Molecular energy is quantized. The set of quantum states corresponding to possible energy levels ϵ_i determines the spectrum. Therefore, by studying the spectrum one can obtain an idea about the energy levels of molecules. But in order to estimate the energy of a system, one must further know how the molecules are distributed in these levels. The energy distribution of molecules is described by the exponential Maxwell-Boltzmann exponential law: $n_i = n_0 e^{-\epsilon_i/kT}$. The state δ_i can be achieved in several ways, therefore it is assigned the statistical weight g_i.

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The quantity $Q = \sum g_i e^{-\frac{\epsilon_i}{kT}}$, characterizing overall the possible energy levels and the distributions of molecules therein obviously completely determines the energy state of the system. This quantity is called the statistical sum, the sum of states or distribution function.

It can be shown that

$$Z = -RT \ln Q. \tag{I.2}$$

In the general case, the isotopic exchange reaction is written as

$$mAX_n + nBX_m^* \rightleftarrows mA_n^* + nBX_m \tag{I.3}$$

(X is an element, the isotopes of which are being exchanged; the asterisk denotes the heavier isotope).

The equilibrium constant of isotopic exchange, ordinarily, is expressed in terms of the coefficients of the final and initial reaction products:

$$K = \frac{[AX_n^*]^m [BX_m]^n}{[AX_n]^m [BX_m^*]^n}. \tag{I.4}$$

Under Eq. (I.1), we have

$$RT \ln K = -mZ_{AX_n^*} - nZ_{BX_m} + mZ_{AX_n} + nZ_{BX_m^*}$$

or, with reference to Eq. (I.2),

$$\ln K = m \ln Q_{AX_n^*} + n \ln Q_{BX_m} - m \ln Q_{AX_n} - n \ln Q_{BX_m^*}.$$

Therefore,

$$K = \left(\frac{Q_{AX_n^*}}{Q_{AX_n}}\right)^m \Big/ \left(\frac{Q_{BX_m^*}}{Q_{BX_m}}\right)^n. \tag{I.5}$$

The energy of molecules can be represented as the sum of energy terms: $\epsilon = \epsilon_{transl} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{el} + \epsilon_o$, where the subscripts refer to the translational, rotational, and vibrational energy motion, to the energy of electronic excitation, and ϵ_o is the zero point energy.

In view of the exponential nature of the dependence of Q on ϵ, the distribution function will be expressed by the product of the cofactors: $Q = Q_{transl} \cdot Q_{rot} \cdot Q_{vib} \cdot Q_{el} E^{-\frac{\epsilon_o}{kT}}$. /12

The distribution functions for the electronic levels drop out of the calculation, since Q_{el} are virtually identical for isotopes.

For the other distribution functions, the following relations are known:

$$Q_{transl} = \text{const} \frac{m^{3/2} T^{3/2}}{p}, \tag{I.6}$$

where m is the molecular mass and p is the pressure or concentration;

$$Q_{rot} = \text{const} \frac{IT}{s}, \tag{I.7}$$

where s is the symmetry number of the molecule, and I is the moment of inertia; and

$$Q_{vib} = \prod_{i}^{3N-6} \left(\frac{1}{1 - e^{-h\nu_i / kT}} \right), \tag{I.8}$$

where ν_i is the vibrational frequency.

The vibrational energy ϵ_{vib} is associated with the frequency by the relation

$$\epsilon_{vib} = h\nu \left(n + \frac{1}{2} \right), \tag{I.9}$$

where n is the quantum number corresponding to the number of the energy level and h is Planck's constant.

The ground-level vibrational frequencies correspond to a transition from the lowest energy level at which the molecules have the so-called "zero" energy $\epsilon_o = \frac{1}{2} h\nu$, to a level with quantum number n = 1. Translational and rotational energies when T = 0 are equal to zero, therefore the zero-point energy ϵ_o consists only of the zero-point vibrational energy.

For the relationship between the distribution functions of the isotopic species of molecules, based on Eqs. (I.6), (I.7), and (I.8), and employing the rule for the product of frequencies from the Teller-Redlich theorem, we get:

$$\frac{Q_{AX_n^*}}{Q_{AX_n}} = \frac{s}{s^*} \prod_{i}^{3N-6} \frac{\nu_i^* e^{-\frac{h\nu_i^*}{2kT}} \left(1 - e^{-\frac{h\nu_i}{kT}} \right)}{\nu_i e^{-\frac{h\nu_i}{2kT}} \left(1 - e^{-\frac{h\nu_i^*}{kT}} \right)}. \tag{I.10}$$

Usually the notation $u_i = \frac{h\nu_i}{kT}$, is introduced, and with reference to the relation $\operatorname{sh} x = \frac{e^x - e^{-x}}{2}$, Eq. (I.10) is transformed as follows:

$$\frac{Q_{AX_n^*}}{Q_{AX_n}} = \frac{s}{s^*} \prod_i^{3N-6} \frac{u_i^* \operatorname{sh} \frac{u_i}{2}}{u_i \operatorname{sh} \frac{u_i^*}{2}}. \qquad \text{(I.11)}$$ /13

A quantity equal to the root, whose degree is determined by the number of atoms replaced in the isotopic species, of the product appearing in the right-hand part of Eq. (I.11), Ya. M. Varshavskiy and S. E. Vaysberg /6/ have suggested calling the β-factor, that is,

$$\frac{Q_{AX_n^*}}{Q_{AX_n}} = \frac{s}{s^*} \beta_{AX_n}^n. \qquad \text{(I.12)}$$

Hence, with reference to Eq. (I.5), the equilibrium constant of the overall isotope-exchange reaction (I.3) is expressed as follows:

$$K = \frac{\left(\frac{s}{s^*}\right)_{AX_n}^m}{\left(\frac{s}{s^*}\right)_{BX_m}^n} \frac{\beta_{AX_n}^{mn}}{\beta_{BX_m}^{nm}}. \qquad \text{(I.13)}$$

The symmetry number is equal to the number of indistinguishable positions that molecules can occupy in space and is easily established from geometrical considerations.

Thus, the thermodynamic isotope effect is entirely determined by the ratio of β-factors, which in turn are functions of temperature and of vibrational frequencies.

As we know, simple concentration relations like (I.4) are applicable only for ideal gases and solutions. In real systems, in place of the concentrations use is made of activities obtained by multiplying the concentration by some activity coefficient, which is a function of all concentrations and of the temperature. The characteristic difference of isotope exchange reactions is that even when there is a considerable deviation in the conditions in which they occur from ideal-gas laws, simple concentration relationships are preserved, since the activities, being functions of element concentrations, are shortened in the expression for the constant.

It should be noted that the distribution function must include a cofactor that takes account of the presence of nuclear spin and its effect on rotational levels:

$$Q_{\text{rot.spin}} \quad Q_{\text{rot}} Q_{\text{spin}} = Q_{\text{rot}} (2\sigma_i + 1),$$

where σ_i is the quantum spin number and i is the number of atoms in the molecule.

Each nucleus has an internal momentum, which interacts with the momenta of the electrons of other nuclei. It is measured in the units h and, under quantum mechanics, can take on integral (or zero) and semiintegral values.

The spin of a nucleus is equal to the vector sum of the spins of its constituent particles, therefore if the sum of protons and neutrons (with semiintegral spin) are equal to an even number, the nucleus spin is equal to an integer or zero. In nuclear systematics, the folllowing rule obtains: all e.e. nuclei have $\sigma = 0$, and o.o. nuclei have a spin expressed by an integer, while nuclei of the o.e. and e.-o types have a spin that is a multiple of ½. In particular, the nucleus ${}_6C^{12}$ has a spin of zero, and the nucleus ${}_6C^{13}$ has $\sigma = ½$. Therefore, the distribution functions of isotopic molecules must differ by a factor that takes into account the difference in the nuclear spins of the isotopic molecules. /14

However, to a sufficiently exact approximation it can be assumed that an atom has an identical spin, regardless of whether it is in the free state or part of some chemical compound, therefore the β-factors of any compounds of a given element will include the same correction for the difference in nuclear spins of the isotopes (if this is involved), and in the expression determining the equilibrium constant the corresponding coefficients will be shortened:

$$\alpha = \frac{\gamma_{\text{nucl. spin}}\, \beta_{AX_n}}{\gamma_{\text{nucl. spin}}\, \beta_{BX_m}} = \frac{\beta_{AX_n}}{\beta_{BX_m}}.$$

Thus, the difference in isotope spins to the first approximation does not affect isotope fractionation in chemical processes. However, it must be borne in mind that the nuclei with spin of zero and with semiintegral spin interact differently with an applied magnetic field and theoretically one can anticipate isotope effects of this kind. This problem has gone virtually unstudied. Chemical thermodynamics of isotopes examines the fractionation of isotopes only as a function of ground-level vibrational frequencies and temperatures. We note that the presence of a semiintegral spin for the nucleus of the heavy carbon isotope permits employing the methods of nuclear magnetic

resonance (C^{13}-NMR-spectroscopy) in investigating the composition and structure of organic compounds /118/.

Relationship Between Equilibrium Constants of Isotope Exchange Reactions and the Partition Coefficients of Isotopes in Systems Containing Polyatomic Atoms

The isotope exchange reaction is

$$mAX_n + nBX_m^* \rightleftarrows AX_n^* + nBX_m, \qquad (I.14)$$

where X* and X are the heavy and light isotopes of a given element, respectively, which is characterized by the equilibrium constant expressed in terms of the ratio of the concentrations of the isotopic species (I.4). However, in contrast to element exchange reactions where the concentrations of all reactants can be measured separately, in the case of isotope exchange only the isotopic composition of the components can be determined experimentally: $(X^*/X)_{AX_n} : (X^*/X)_{BX_m}$. The value of this ratio is called the partition coefficient of the isotopes of the isotopic exchange reaction and can be expressed in terms of the ratios of the sums of concentrations of isotopic species as follows: /15

$$\alpha = \frac{n[AX_n^*] + \ldots + (n-i)[AX_iX_{n-i}^*]}{n[AX_n] + \ldots + (n-i)[AX_i^*X_{n-i}]} \Big/ \frac{m[BX_m^*] + \ldots + (m-j)[AX_jX_{m-j}^*]}{m[BX_m] + \ldots + (m-j)[AX_j^*X_{m-j}]}, \qquad (I.15)$$

where i and j are the numbers of the replaced atoms in the isotopic species of the corresponding compounds.

For carbon, we have

$$\alpha = (C^{13}/C^{12})_{AX_n}/(C^{13}/C^{12})_{BX_m} \simeq 1 \quad (\delta C^{13}_{AX_n} - \delta C^{13}_{BX_m}) \cdot 10^{-2}. \qquad (I.16)$$

It is not α that is determined by the methods of statistical thermodynamics and the theory of vibrations, that is, directly by calculation, but the equilibrium constant K. Thus, comparing the observed (experimentally measured) isotope effects with the theoretical, underlying the basis of the geochemical application of the isotope method, can be realized if we know the form of the relationship between α and K.

In the simplest case when m = n = 1, as follows from comparing Eqs. (I.4) and (I.15), α in magnitude coincides with K. Obviously, for this reason often in the geochemical literature no distinction is made between these two parameters. But in the case of systems containing polyatomic compounds, the relationship between the partition coefficient and the equilibrium constant is more complicated.

If compounds contain several replaceable atoms, then in the reaction (I.14) several particular reactions of isotopic species take place:

$$AX_{n-i+1}X^*_{i-1} + BX_{m-j}X^*_j \rightleftarrows AX_{n-i}X^*_i + BX_{m-j+1}X^*_{j-1}, \tag{I.17}$$

each of which is characterized by the equilibrium constant:

$$K_{ij} = \frac{[AX_{n-i}X^*][BX_{m-j+1}X^*_{j-1}]}{[AX_{n-i+1}X^*_{i-1}][BX_{m-j}X^*_j]}, \tag{I.18}$$

where the equilibrium constant of the isotope exchange reaction of the completely isotope-replaced species (I.14) is equal to the product of the reaction constants of the isotope species:

$$K = \frac{[AX^*_n]^m [BX_m]^n}{[AX_n]^m [BX^*_m]^n} = \prod_{i=1}^{n} \prod_{j=1}^{m} K_{ij}. \tag{I.19}$$

Based on the principle of the equiprobable distribution of isotopes that derives from the requirement of an entropy maximum in an equilibrium isotopic mixture, the β-factors of all isotopic species are assumed to be equal: /16

$$\begin{cases} \beta_1 = \beta_2 = \ldots = \beta_i = \ldots = \beta_{AX_n}, \\ \beta_1 = \beta_2 = \ldots = \beta_j = \ldots = \beta_{BX_m}. \end{cases} \tag{I.20}$$

Hence,

$$K = \left(\frac{\beta_{AX_n}}{\beta_{BX_m}}\right)^{mn} \prod_{i=1}^{n} \prod_{j=1}^{m} \left(\frac{s}{s^*}\right)_i \left(\frac{s^*}{s}\right)_j. \tag{I.21}$$

The product in the right-hand part is denoted by K_o. Then,

$$\frac{\beta_{AX_n}}{\beta_{BX_m}} = \sqrt[mn]{K/K_0}. \tag{I.22}$$

It was shown that when there is an equiprobable distribution of isotopes in different isotopic species, the partition coefficient of the isotopes is determined by the relation /5/

$$\alpha = \sqrt[mn]{K/K_0} \tag{I.23}$$

and, therefore,

$$\alpha = \frac{\beta_{AX_n}}{\beta_{BX_m}}. \tag{I.24}$$

In view of the condition (I.20), α is determined in terms of the β-factor of any isotopically-replaced species, most often a completely isotopically-replaced species. For example, the thermodynamic isotope effect in the CO_2-H_2O system with respect to oxygen can, with the same result, be calculated either as the species $CO^{16}O^{18}$, or as the species $CO^{18}O^{18}$.

The condition of equiprobable distribution of isotopes, which is the basis of the derivation of the above-presented relations, is usually assumed by starting from the fact that isotope distribution does not depend on the degree of isotopic replacement, in other words, the equilibrium of the exchange of the i-th atom does not depend on whether the remaining n - 1 atoms are the isotopes X or X*. The latter is valid virtually for all kinds of isotope exchange, with the exception of hydrogen-deuterium exchange in low-molecular compounds of hydrogen, where owing to the large relative difference in the mass of the hydrogen isotopes, during replacement there is a considerable redistribution of the masses in the molecule, disrupting the additivity of the isotopic replacement.

In the more general case, the condition of equiprobable distribution of isotopes must be supplemented by the requirement of the equivalents of the exchangeable atoms in the molecule. The point is that in some compounds, whose typical representatives /17 include hydrocarbons, not only does the molecule contain several replaceable atoms, but the atoms themselves occupy in it non-equivalent positions. From analogy with the ideas developed in the theory of the vibrations of molecules, obviously equivalent atoms must be the term used to denote atoms converting one into the other in any symmetry operations that the molecule is subjected to .

Let us take, for example, the propane molecule. The solution of the vibrational problem and quantum-statistical calculation for the propane molecule (see below) shows that the β-factor calculated for replacement at a central atom (see Fig. 4) is not equal to the β-factor calculated for replacement at a peripheral atom, although the β-factors are the same for both peripheral atoms (see Table 4).

Thus, in the case of polyatomic compounds containing non-equivalent atoms, the partition coefficient no longer can be expressed simply by the ratio of the β-factors, by taking the β-factors of any isotopically replaced species, for example, completely isotopically replaced species.

A problem arises: find an expression relating α to the β-factors in the event that a molecule contains nonequivalent atoms.

Then, by neglecting in Eq. (I.25) the terms containing 1/R, we arrive at the simpler approximation:

$$\alpha \simeq \frac{\beta_I + 2\beta_{II}}{3} \frac{1}{\beta_{CH_4}}. \qquad (I.26)$$

On analyzing the general properties of Eq. (I.25), it is not difficult in the same approximation to generalize Eq. (I.26) to the case of the exchange of molecules having arbitrary composition:

$$\alpha = \frac{m \sum_i^{q_A} p_A (\beta_{AX_n})_i}{n \sum_j^{q_B} p_B (\beta_{BX_m})_j}. \qquad (I.27)$$

The summation is carried out over the numbers of the q_A- and q_B-groups of the equivalent atoms; p_A and p_B are the numbers of the equivalent atoms in each q_A- and q_B-group appearing as part of the molecules being exchanged. These numbers are equal to the ratio of the symmetry numbers of the unreplaced molecule and the molecule replaced at one of the exchangeable atoms.

From Eq. (I.27) it follows that to describe the equilibrium of the isotopic exchange, each molecule containing nonequivalent exchangeable atoms must be characterized by the number of β-factors equal to the number of the groups of equivalent atoms in the molecule.

A polyatomic compound containing n exchangeable atoms has a number of isotopic species and, therefore, β-factors which is equal to

$$\sum_{i=1}^{n} i! \frac{n!}{(n-i)!}, \qquad (I.28).$$

where i is the degree of isotopic replacement. For example, for pentane this number is 31. Still, q = 3 β-factors is sufficient for the isotopic characterization of pentane, according to Eq. (I.27). These β-factors correspond to singly isotopically-replaced species characterizing the independent symmetry types of the isotopic species in a given compound, that is, groups of equivalent atoms. Let us denote them by β_q (we will number q in distinction to i with Roman numerals) and let us call the isotopic species the thermodynamic isotopic factors. /19

As follows from the familiar relations /40/ the β-factors of all the remaining isotopic species of a compound are not independent

Before us this problem did arise when we set out to calculate the partition coefficients of isotopes in hydrocarbon systems. It must be stated that hydrocarbons, just like any organic compound, represent the most widespread and typical examples of polyatomic isotopically-nonequivalent compounds. Deriving the appropriate formula for the relationship of α with the β-factors was done by us earlier /4/.

Even for the simple system of propane-methane, in general form a quite cumbersome expression results:

$$\alpha = \frac{\beta\left[3\frac{\beta^2}{\beta^2_{CH_4}}\cdot\frac{1}{R^2}+\frac{2\beta^3_{II}+4\beta^3}{\beta\beta_{II}}\cdot\frac{1}{\beta_{CH_4}R}+\frac{1}{\beta}(\beta_I-2\beta_{II})\right]}{\beta_{CH_4}\left[\frac{2\beta^3-\beta^3_{II}}{\beta_{II}}\cdot\frac{1}{\beta^2_{CH_4}R^2}+\frac{2\beta_I-4\beta_{II}}{\beta_{CH_4}R}+3\right]}, \qquad (I.25)$$

where β, β_I, and β_{II} are the β-factors of the isotopic species of propane, correspondingly completely isotopically replaceable, replaceable at the central atom, and replaceable at the peripheral atom; β_{CH_4} is the β-factor of methane; and R is the isotopic composition of methane. Understandably, included in Eq. (I.25) is a quantity characterizing the isotopic composition of only one of the components, since at the state of equilibrium the isotopic composition of the other component is uniquely determined by the isotopic composition of the former.

Above all we must note that Eq. (I.25) is more general compared with Eq. (I.24) for α in the case of an equiprobable distribution. Actually, if we take condition (I.20) of equiprobability $\beta_I = \beta_{II} = \beta$, we get the relation $\alpha = \beta/\beta_{CH_4}$, analogous to (I.24).

The quantity R appears in Eq. (I.25) for α. Usually it is assumed that the partition coefficient of isotopes α is some quantity characterizing the system and not dependent on the isotopic composition of the components in it. However, in the case of compounds containing nonequivalent, this is not so. For example, if in the experimental determination of α for some system, we use enriched preparations, we get a value that differs from the value characterizing the corresponding isotopically dilute system, in spite of the fact that in either case complete equilibrium can be attained. This is a feature of systems containing polyatomic isotopically-nonhomogeneous (that is, with nonequivalent atoms) compounds. Given the condition of equivalence, in Eq. (I.25) R is shortened and does not disappear from the formula for α. /18

In light elements, the abundance of the light isotope, as a rule, is much higher than for the heavy isotope, that is, $R \gg 1$.

and can be obtained as combinations of thermodynamic isotopic factors β_q. Therefore, in the theoretical analysis of the isotopic properties of a molecule, it is necessary and sufficient to carry out the calculation only of the β_q-factors.

H. Johansen [17,47] computed the quantities $f(\frac{s^*}{s})$ (the product of the ratio of the distribution functions by the ratio of the symmetry numbers), analogous to our β-factors, for all isotopic species of the series of compounds (Table 1); for example, in the propynal molecule (see Fig. 13), all three atoms are nonequivalent. This means that this compound is characterized by three thermodynamic isotopic factors corresponding to the isotopic species: $C_2HC^{13}HO$ (β_I), $C^{13}CHCHO$ (β_{II}), and $CC^{13}HCHO$ (β_{III}). As we can easily see by direct recalculation of the data in Table 1, the remaining β-factors (the quantities $f\frac{s^*}{s}$) are not independent:

$$f_1\frac{s^*}{s}=\beta_I,\quad f_2\frac{s^*}{s}=(\beta_{II}\beta_{III})^{1/2},\quad f_3\frac{s^*}{s}=(\beta_I\beta_{II}\beta_{III})^{1/3},$$

$$f_4\frac{s^*}{s}=\beta_{II},\quad f_5\frac{s^*}{s}=\beta_{III},\quad f_6\frac{s^*}{s}=(\beta_{II}\beta_{III})^{1/2},$$

$$f_7\frac{s^*}{s}=\beta_I\quad f_8\frac{s^*}{s}=(\beta_I\beta_{III})^{1/2}.$$

In other words, the β-factor of any multiple substituted isotopic species is defined as the geometric mean of the β-factors characterizing all singly-isotopic replacements in the given species:

$$\beta_{AX_{n-i}X_i^*}=\left(\prod^{i}\beta_i\right)^{1/i}. \qquad (I.29)$$

Since β_i-factor is equal to any β_q-factor, then

$$\beta_{AX_{n-i}X_i^*}\quad\left(\prod\beta_{q_i}^{p_i}\right)^{1/i}, \qquad (I.30)$$

where p_i characterizes the multiplicity of the repetition of the β_q-factor determined by the number of equivalent atoms appearing in the given isotopic species. As for the completely isotopically-replaced species, we have /21

$$\beta^*_{AX_n}=\left(\prod^{i=n}\beta_i\right)^{\frac{1}{n}}=\left(\prod^{q}\beta_{q_i}^{p_i}\right)^{\frac{1}{n}}. \qquad (I.31)$$

TABLE 1. VALUES OF f(s*/s)OF ISOTOPIC SPECIES OF SEVERAL ORGANIC /20
AFTER H. JOHANSEN /1747

PROPYNAL C_2HCHO

T, K	$f_1\frac{s^*}{s}$ $\frac{C_2HC^{13}HO}{C_2HC^{12}HO}$	$f_2\frac{s^*}{s}$ $\frac{C_2^{13}HCHO}{C_2^{12}HCHO}$	$f_3\frac{s^*}{s}$ $\frac{C_2^{13}HC^{13}HO}{C_2^{12}HC^{12}HO}$	$f_4\frac{s^*}{s}$ $\frac{C^{13}CHCHO}{C^{12}CHCHO}$	$f_5\frac{s^*}{s}$ $\frac{C_2^{13}HCHO}{C^{13}CHCHO}$	$f_6\frac{s^*}{s}$ $\frac{C_2^{13}HC^{13}HC}{C_2HC^{13}HC}$	$f_7\frac{s^*}{s}$ $\frac{C_2^{13}HC^{13}HO}{C_2^{13}HCHO}$	$f_8\frac{s^*}{s}$ $\frac{C_2^{13}HC^{13}HO}{C^{13}CHCHO}$
273°.15	1.196	1.282	1.537	1.133	1.132	1.285	1.199	1.317
300	1.170	1.246	1.461	1.117	1.116	1.248	1.173	1.308
350	1.134	1.196	1.359	1.094	1.093	1.198	1.136	1.242
400	1.109	1.160	1.288	1.078	1.077	1.162	1.110	1.195
450	1.090	1.134	1.238	1.066	1.064	1.135	1.091	1.161
500	1.076	1.114	1.199	1.056	1.055	1.115	1.077	1.136

TABLE 1 /conclusion/

ACETALDEHYDE CH_3CHO

T, K	$\frac{CH_3CHO^{17}}{CH_3CHO^{16}}$	$\frac{CH_3CHO^{18}}{CH_3CHO^{16}}$	$\frac{CD_3CHO}{CH_3CHO}$	$\frac{CH_3CDO}{CH_3CHO}$	$\frac{CD_3CDO}{CH_3CHO}$
273.15	1.052	1.097	3155.89	10.201	32749.72
300	1.045	1.084	1262.27	7.792	9988.92
350	1.036	1.066	337.99	5.298	1813.86
400	1.029	1.054	127.82	3.991	515.76
450	1.024	1.044	60.82	3.218	197.57
500	1.020	1.037	33.97	2.720	93.15

The rules (I.29)-(I.31) are strictly satisfied also for β-factors, even those differing widely from unity, for example, the β-factors of the deuterium-substituted forms of acetic aldehyde (see Table 1).

The reduced sum appearing in the numerator and denominator of Eq. (I.27) and representing a combination of thermodynamic isotopic factors of the isotopic forms, we will call the molecular thermodynamic isotopic factor or the thermodynamic isotopic factor of the compound:

$$\beta_\Sigma = \frac{1}{n}\sum^{q} p_A\beta_i. \qquad (I.32)$$

Then α again will represent the ratio of β-factors, where the reduced β_Σ-factors of the compounds constituting the system are given in the numerator and the denominator:

$$\alpha = \frac{\beta_{\Sigma_{AX_n}}}{\beta_{\Sigma_{BX_m}}}. \qquad \text{(I.33)}$$

Principles of Calculating Isotopic Frequencies

The vibrational frequencies of the basic and isotopically substituted species of the molecules under study required for calculation of β-factors in principle can be obtained experimentally from the combination scattering spectra and the infrared spectra of the corresponding compounds. However, spectroscopic data on frequencies, especially of polyatomic and highly symmetric molecules, are incomplete, and isotopic frequency shifts for elements heavier than hydrogen are small and they are difficult to measure with adequate precision. Therefore to calculate the β-factors, use is made of the theoretically established isotopic frequencies.

Methods of the theory of vibrations underlying the calculation of isotopic frequencies are quite well elaborated. Great credit in developing these methods belongs to the representatives of the Soviet school of spectroscopists: M. V. Vol'kenshteyn, M. A. Yel'yashevich, L. S. Mayanets, B. I. Stepanov, and so on. In fundamental works [21, 83], and also in a series of handbooks and monographs [13, 51, 84, 105], the theory of molecular vibrations is set forth in relation to its applications in spectroscopy and physical chemistry. Calculations of the isotopic frequencies have attracted much less attention, principally owing to the interpretation of spectra and to a lesser extent, for the purpose of calculating the thermodynamic isotopic effects. Among the latter, there is a predominance of studies on various compounds of interest from the standpoint of the techniques of isotope separation. /22

As for the study of isotope effects in reactions typical of natural conditions, as far as we know, no special work in this direction has been carried out and geochemists have had to be content with the isotopic constants that were calculated in various instances.

Considering this circumstance, it is expedient to preface the presentation of information on the thermodynamic isotopic factors of molecules with a brief introduction touching on the main principles of the calculation of isotopic frequencies, including the aspects in which they are of interest to isotopists-geochemists.

Secular Equation

Since the energy states of molecules are quantized, solving the problem of their fluctuations rigorously can be carried out by means of the Schroedinger equation, which is the fundamental quantum-mechanical equation of motion. However, the solution to Schroedinger's equation for polyatomic molecules presents nearly insurmountable mathematical difficulties. Therefore the vibrational problem with some approximation, which however, is quite good for vibrations of small amplitude, is solved within the frame of reference of classical physics, in which motion, including vibrational motion of a molecule, is described as we know by Newton's second law:

$$m\frac{d^2x}{dt^2}-\varphi=0. \qquad (I.34)$$

The force ϕ, which has the significance of a quasielastic force restraining atoms in the equilibrium position, can be regarded as the result of a change in some potential function (potential energy) V, therefore:

$$m\frac{d^2x}{dt^2}+\frac{\partial V}{\partial x}=0. \qquad (I.35)$$

The explicit form of the dependence of the potential function on coordinates is impossible to specify. We can only indicate some common properties of it. The potential function describing the interaction of atoms is a function of all coordinates. A molecule containing N atoms has 3N degrees of freedom and must be described by 3N coordinates, that is $V=\sum_{i}^{3N}V(x_i)$. By x_i we mean /23 the Cartesian ccordinates of the displacement of atoms from the equilibrium position, that is, $x_1=\Delta x_1, x_2=\Delta y_1$, $x_3 = z_1$ for the first atom m_1; $x_4=\Delta x_2, x_5=\Delta y_2, x_6=\Delta z_2$ -- for the second atom m_2, and so on. Since interatomic forces ensure preservation of the molecule's configuration -- they restrain the atoms about some equilibrium position, then obviously in this equilibrium position the potential function must be equal to zero: $(V_0)_{x_i=0}=0$, and when the atoms are displaced from the equilibrium position -- -- the potential function must increase in proportion to the displacement. This means that when $x_i = 0$, the potential function not only equals zero, but is also extremal (minimal), that is, its first derivative is equal to zero: $\left(\frac{\partial V}{\partial x_i}\right)_{x_i=0}=0$.

Like any continuous function that has all its derivatives, the potential function can be expanded in a Taylor series, a particular case of which (if the expansion is carried out when the value of the argument is zero, that is, $x_i = 0$) is the Maclaurin series:

$$V_{(x_i)} = V_0 + \sum_{i}^{3N} \left(\frac{\partial V}{\partial x_i}\right)_0 x_i + \frac{1}{2} \sum_{ij}^{3N} \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_0 x_i x_j + \ldots + \\ + \frac{1}{n!} \sum_{ij\ldots n}^{3N} \frac{\partial^{(n)} V}{\partial x_i \partial x_j \ldots \partial x_n} x_i x_j \ldots x_n. \tag{I.36}$$

The first and second terms of this expansion, according to the foregoing, are equal to zero. Neglecting the terms containing derivatives of the third and higher orders, we get the potential function in the so-called quadratic form:

$$V = \frac{1}{2} \sum_{ij}^{3N} \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_0 x_i x_j = \frac{1}{2} \sum_{ij}^{3N} f_{ij} x_i x_j, \tag{I.37}$$

where f_{ij} has the significance of the rate of change in the potential function near the equilibrium position and is called the force constant.

Substituting Eq. (I.37) into Eq. (I.35), we get:

$$m \frac{d^2 x_i}{dt^2} + \frac{\partial}{\partial x} \left[\frac{1}{2} \sum_{i}^{3N} f_{ii} x_i^2 + \frac{1}{2} \sum_{j}^{3N} f_{ij} x_i x_j\right] = 0. \tag{I.38}$$

Eq. (I.38) is satisfied for each atom, coordinate by coordinate. Therefore, we get 3N independent equations of the form /24

$$3N \begin{cases} m_1 \ddot{x}_1 + f_{11} x_1 + f_{12} x_2 + f_{13} x_3 + \ldots + f_{1 \cdot 3N} x_{3N} = 0, \\ m_1 \ddot{x}_2 + f_{22} x_2 + f_{21} x_1 + f_{23} x_3 + \ldots + f_{2 \cdot 3N} x_{3N} = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ m_N \ddot{x}_{3N} + f_{3N\,3N} x_{3N} + \sum_{j}^{3N-1} f_{3N\,j} x_j = 0. \end{cases} \tag{I.39}$$

Each of these equations is a second-order linear differential equation, whose solution is sought for in the form

$$x_i = A_i \cos(\sqrt{\lambda}\, t + \varepsilon), \tag{I.40}$$

where $\lambda^2 = 2\pi\nu$ (ν is the frequency of vibrations).

Substituting this solution into the system of differential equations (I.39) yields the system of algebraic equations:

$$\begin{aligned}
&\left(\frac{1}{m_1}f_{11}-\lambda\right)A_1+\frac{1}{m_1}f_{12}A_2+\ldots+\frac{1}{m_1}f_{1N}A_N=0;\\
&\frac{1}{m_1}f_{21}A_1+\left(\frac{1}{m_1}f_{22}-\lambda\right)A_2-\ldots+\frac{1}{m_1}f_{2N}A_N=0;\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&\frac{1}{m_N}f_{3N\cdot1}A_1+\frac{1}{m_N}f_{3N}A_2+\ldots+\left(\frac{1}{m_N}f_{3N\cdot3N}-\lambda\right)A_N=0.
\end{aligned} \tag{I.41}$$

This system of equations, like the obvious solution $A_i = 0$, corresponding to the absence of vibrations, has 3N solutions, if the determinant of the system is equal to zero:

$$\begin{vmatrix}
\frac{1}{m_1}f_{11}-\lambda & \frac{1}{m_1}f_{12} & \cdots & \frac{1}{m_1}f_{1N}\\
\frac{1}{m_1}f_{21} & \frac{1}{m_1}f_{22}-\lambda & \cdots & \frac{1}{m_1}f_{2N}\\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
\frac{1}{m_N}f_{3N\cdot1} & \frac{1}{m_N}f_{3N\cdot2} & \cdots & \frac{1}{m_N}f_{3N\cdot3N}-\lambda
\end{vmatrix}=0. \tag{I.42}$$

Determinant (I.42) in expanded form is a polynomial of order 3N in λ. Finding the vibrational frequencies reduces to finding 3N roots of λ of Eq. (I.42), which is called the secular equation.

Vibrational motion of a molecule is characterized by the vibration frequencies ν_i, whose number corresponds to the number of degrees of freedom. Each atom executes a complex motion, including vibrations simultaneously in all frequencies ν_i, or as it is phrased, a superpositioning of the vibrational motions of the entire set ν_i characterizing the molecule. Therefore in the general case each of the ground-level frequencies cannot be related to a specific bond, atom, or group of atoms in the molecule. However, the vibrations are executed with different amplitudes so that for a given bond there may be the most well-defined vibration with some single frequency, which is taken as the characteristic frequency for the given bond.

Vibrations which in total describe the vibrational motion of the molecule are called normal vibrations. Possible normal vibrations are established as follows. The molecule is considered as a rigid elastic structure -- the atoms are joined by rigid rods. Normal vibrations correspond to the directions of the deforming (compressive and elongating along the bonds and deforming the angle between the bonds) forces, whose resultant is equal to zero, that is, the forces must not bring the molecule as a whole into translational or rotational motion (Fig. 1).

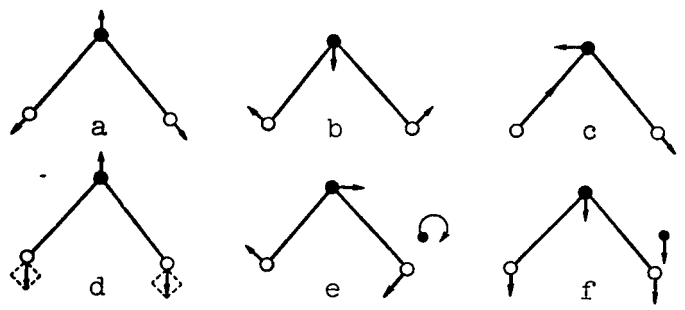

Fig. 1. Vibrational motion of a molecule
a. Normal vibration (elongation of both bonds -- decrease of angle) and reverse motion
b. Normal vibration (compression of both bonds -- increase in angle)
c. Normal vibration (one bond is elongated, the other is compressed -- the angle is not deformed)
d. Dependent vibration, which can be reduced to a vibration of types a and b
e. The resultant of the forces is not equal to zero -- the molecule acquires rotational motion
f. As above, the molecule acquires translational motion

The above-presented equation (I.42) was obtained by neglecting the derivatives of the third and higher orders in the expression for the potential function (I.36). The deviation of an actual vibration from the harmonic corresponding to the potential function, taken in the quadratic form, is small, but it causes a deviation between the calculated and spectrally observed frequencies. Allowing for anharmonicity in the general case is a highly complicated problem. But there are approximate methods. The most common, in particular suitable for calculating isotope effects for carbon, is the method of introducing the spectroscopic mass of hydrogen, that is, using in the calculations not the actual atomic mass of hydrogen atoms of $m_H = 1.008$, but the value $m_H = 1.088$.

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Matrical Representation of Secular Equation

We must say something about the mathematical apparatus used. The motion of a system with N degrees of freedom is described by N coordinates. Thus, the mathematical content of the problem reduces to setting up and solving N linear equations. Here in the course of the solution it becomes necessary to linearly transform the coordinates, for example, in converting from Cartesian coordinates in which the expression is given for the kinetic and potential energies, to the so-called internal coordinates, which are changes in the valency bonds and angles.

The best mathematical apparatus adapted for carrying out operations involved in solving linear equations and linear transformations is matrix calculus. Therefore we will give the following exposition in the terms of matrix algebra. Further, molecules are geometrical figures exhibiting a certain symmetry, where the symmetry operations, that is, the operations of rotation about the symmetry axes, reflection in the planes and in the center of symmetry leading to nondistinguishable spatial configurations of the molecule, constitute a group. In other words, the symmetry operations satisfy the conditions defining the mathematical concept of a group, namely: 1) successive carrying out of two symmetry operations constitutes one of the possible symmetry operations, which is equivalent to the group postulate: the product of two elements of a group is also an element of a group; 2) identity and inverse symmetry operations are possible, corresponding to a unit and inverse element of a group; and 3) the associative law is satisfied, though the commutative law in the general case does not obtain. The theory of groups and matrix calculus are the basis of the mathematical apparatus used in solving problems on the vibrations of molecules within classical physics.

Eq. (I.36) for potential energy in the internal coordinates q

$$2V = \sum_{i,j}^{n} F_{ij} q_i q_j \qquad \text{(I.43)}$$

can be represented in matrical form as follows: /27

$$2V = \tilde{\mathbf{R}} \mathbf{F} \mathbf{R}, \qquad \text{(I.44)}$$

where **R** is the column matrix of the internal coordinates of the form

$$\mathbf{R} \quad \begin{vmatrix} q_1 \\ q_2 \end{vmatrix}.$$

The internal coordinates employed in the theory of molecular vibrations instead of Cartesian coordinates are changes in the length of the valency bonds and in the size of angles; $\tilde{\mathbf{R}}$ is a transposed **R**-matrix, that is, matrix in which the columns are interchanged with the rows.

In this case,

$$\tilde{\mathbf{R}} \cdot \; | q_1 q_2 q_3 \ldots |.$$

The matrix of the force constants **F** is such that

$$2V = \left| q_1 q_2 q_3 \ldots \right| \left| \begin{array}{l|l} F_{11}F_{12}F_{13}\ldots & q_1 \\ F_{21}F_{22}F_{23}\ldots & q_2 \\ F_{31}F_{32}F_{33}\ldots & q_3 \\ \cdots\cdots & \vdots \\ \cdots\cdots & \vdots \end{array} \right|. \qquad \text{(I.45)}$$

Actually, as we know, the elements $\{C\}_{ij}$ of some matrix **C**, the product of matrices **A** and **B**, found by the following law:

$$\{C\}_{ij} = \sum_{k}^{n} \{A\}_{ik} \{B\}_{kj}, \qquad \text{(I.46)}$$

where i is the row number; j is the column number; and k changes from 1 to n, equal to the matrix order.

Therefore

$$\mathbf{FR} = \left| \begin{array}{l} \{F_{11}q_1 \quad F_{12}q_2 + F_{13}q_3 \ldots\} \\ \{F_{21}q_1 + F_{22}q_2 + F_{23}q_3 \ldots\} \\ \{F_{31}q_1 + F_{32}q_2 + F_{33}q_3 \ldots\} \\ \cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots \end{array} \right| \qquad \text{(I.47)}$$

and

$$\tilde{\mathbf{R}}\mathbf{FR} = F_{11}q_1q_1 + F_{12}q_2q_1 + F_{13}q_3q_1 + \ldots + F_{22}q_2q_2 + F_{23}q_3q_2 +$$
$$+ F_{21}q_1q_2 + \ldots + F_{31}q_1q_3 + F_{32}q_2q_3 + F_{33}q_3q_3 + \ldots = \sum_{i,j=1}^{n} F_{ij}q_iq_j.$$

The elements $\{F\}_{ij}$ of matrix **F** are force constants or the coefficients of the dynamic interaction of the internal coordinates. /28

Similarly, we can represent in matrical form the expression for the kinetic energy /13/:

$$2W = \tilde{\dot{\mathbf{R}}}\mathbf{G}^{-1}\dot{\mathbf{R}}, \qquad \text{(I.48)}$$

where $\mathbf{G}^{-1}$ is the matrix that is the inverse of the **G**-matrix.

The elements of the inverse matrix are determined by employing the rule of matrix multiplication (I.46) from the following relation:

$$\mathbf{G}^{-1}\mathbf{G} = \mathbf{I}, \tag{I.49}$$

where **I** is the unit matrix of the form

$$\begin{vmatrix} 100\ldots \\ 010\ldots \\ 001\ldots \\ \ldots\ldots \end{vmatrix}$$

In the theory of molecular vibrations, rules are established by which the elements $\{G\}_{ij}$ of the matrix G can be found /21/. Elements of the G-matrix, also bearing the name coefficients of the kinematic interaction of internal coordinates, are ultimately determined by the molecular configuration and the masses of the atoms comprising the molecule.

If in Lagrange's equation

$$\frac{d}{dt}\left(\frac{\partial W}{\partial \dot{\mathbf{R}}}\right) + \frac{\partial V}{\partial \mathbf{R}} = 0, \tag{I.50}$$

which is Newton's equation (I.34) solved for the potential and kinetic energies, we substitute Eqs. (I.44) and (I.48) for V and W, the corresponding secular equation will be of the form

$$|\mathbf{F} - \mathbf{G}^{-1}\lambda| = 0 \tag{I.51}$$

or after multiplying it by matrix G

$$|\mathbf{GF} - \mathbf{I}\lambda| = 0. \tag{I.52}$$

The latter is the most compact notation of the secular equation in matrical form.

In order to obtain the elements $\{GF\}_{ij}$ of the matrix of the secular equation, the F- and G-matrices are multiplied together by the rule of matrix multiplication:

$$\{GF\}_{ij} = \sum_{k}^{n} G_{ik}F_{kj}. \tag{I.53}$$

Since in the general case the matrices do not commutate, that is, $GF \neq FG$, this order of multiplication of cofactors must be rigorously observed. /29

By multiplication, one gets an equation in the matrical form

$$\begin{vmatrix} \sum_k^n G_{1k}F_{k1} - \lambda & \sum_k^n G_{1k}F_{k2} & \sum_k^n G_{1k}F_{k3} \dots \\ \sum_k^n G_{2k}F_{k1} & \sum_k^n G_{2k}F_{k2} - \lambda & \sum_k^n G_{2k}F_{k3} \dots \\ \sum_k^n G_{3k}F_{k1} & \sum_k^n G_{3k}F_{k2} & \sum_k^n G_{3k}F_{k3} - \lambda \dots \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots \end{vmatrix} = 0, \qquad (I.54)$$

which is wholly analogous to Eq. (I.42).

The elements $\{F\}_{ij}$ are the force constants f_{ij}. In the latter, the subscripts i and j denote the kind of interacting coordinates. Customarily, coefficients corresponding to the interaction of coordinates that do not have common atoms are equal to zero. Owing to the invariance of the potential energy $f_{ij} = f_{ji}$, therefore the number of values of the force constants is smaller than the number of elements of the F-matrix.

Determining the unknown force constants is a purely spectroscopic problem and when the isotopic frequencies are being calculated it can prove necessary only with respect to molecules that have not been studied in terms of vibrations. It must be borne in mind that given the present status of the theory of molecular vibrations, calculation of force constants is based on several assumptions, therefore the proper selection of force constants and the soundness of the assumptions introduced nearly entirely determines the accuracy of the calculation frequencies, and ultimately, of β-factors.

The force constants are determined by starting from the spectroscopically measured frequencies.

Inserting each of the measured frequencies into the secular equation (I.54), we get equations of the type

$$\begin{aligned} &\varphi_1(f_{11}, f_{12}, f_{13}, \dots, f_{nn}) = 0; \\ &\varphi_2(f_{11}, f_{12}, f_{13}, \dots, f_{nn}) = 0; \\ &\dots\dots\dots\dots \\ &\varphi_t(f_{11}, f_{12}, f_{13}, \dots, f_{nn}) = 0, \end{aligned} \qquad (I.55)$$

whose number is equal to the number of the known frequencies. Quite obviously, the number of the unknown force constants is always larger than the number of the known frequencies. The maximum number of frequencies is 3N - 6, while the number of constants is N (N + 1)/2.

Since $\frac{N(N+1)}{2} > 3N - 6$ for all N, it is virtually impossible /30 to determine all the force constants. Therefore one must make the assumptions that several constants are equal to each other, several are negligibly small, and finally several are analogous to the similar constants from other molecules. The indeterminacy can be somewhat reduced (the number of equations for finding the constants can be increased) by involving experimental data on isotopic frequencies. By substituting into the secular equation an isotopic frequency and the coefficients of the kinematic interaction $_{ij}$, appropriately recalculated for the isotopic molecule, one can obtain additional equations of the type (I.55), since the coefficients f_{ij} are identical for the isotopic molecular species. This procedure is particularly effective for hydrogen-containing compounds, since deuterium-substituted molecules yield a significant shift in the isotopic frequency, which can be measured to a fairly high precision. Therefore, and this bears noting, data on the coefficients of the dynamic interaction of hydrogen-containing compounds, in particular, hydrocarbons, are most complete and most reliable.

Finding the roots λ of the secular equation, called the eigenvalues of the matrices, in the case of matrices of high ranks represents a highly laborious procedure, but when computers are used it is a standard mathematical problem and is solved with an electronic computer based on standard programs for finding the eigenvalues of matrices.

Methods have also been developed for solving secular equations, including equations of high degree, manually, without using an electronic computer.

Essentially, the mathematical procedure used to solve the secular equation involves reducing the matrix specifying it to the diagonal form, that is, converting from the matrix

$$\begin{vmatrix} \{GF\}_{11}-\lambda & \{GF\}_{12} & \{GF\}_{13}\dots \\ \{GF\}_{21} & \{GF\}_{22}-\lambda & \{GF\}_{23}\dots \\ \{GF\}_{31} & \{GF\}_{32} & \{GF\}_{33}-\lambda\dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \end{vmatrix}$$

to the matrix

$$\begin{vmatrix} \{GF\}'_{11}-\lambda & 0 & 0 \\ 0 & \{GF\}'_{22}-\lambda & 0\ldots \\ 0 & 0 & \{GF\}'_{31}-\lambda\ldots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix}.$$

Then $\lambda_1 = \{GF\}'_{11};\ \lambda_2 = \{GF\}'_{22};\ \ldots;\ \lambda_n = \{GF\}'_{nn}.$ /31

Converting to the diagonal form of the matrix (determinant) of the secular equation is carried out by introducing intermediate coordinates, which are linear transformations of the initial coordinates such that part of the interaction (part of the nondiagonal elements) tends to zero. Converting to the coordinates of symmetry examined below is one of these procedures of diagonalization of the matrix. Here the matrix is reduced to the so-called quasidiagonal form.

For example, a sixth order secular equation is decomposed into three

$$\begin{array}{c|cccccc} A_{1g} & \{GF\}_{11}-\lambda & \{GF\}_{12} & 0 & 0 & 0 & 0 \\ & \{GF\}_{21} & \{GF\}_{22}-\lambda & 0 & 0 & 0 & 0 \\ A_{2g} & 0 & 0 & \{GF\}_{33}-\lambda & 0 & 0 & 0 \\ & 0 & 0 & 0 & \{GF\}_{44}-\lambda & \{GF\}_{45} & \{GF\}_{46} \\ B_1 & 0 & 0 & 0 & \{GF\}_{54} & \{GF\}_{55}-\lambda & \{GF\}_{56} \\ & 0 & 0 & 0 & \{GF\}_{64} & \{GF\}_{65} & \{GF\}_{66}-\lambda \end{array} = 0$$

blocks of independent equations of second, first, and third order, corresponding to specific classes (types) of symmetry. Here the coefficients corresponding to the interaction of coordinates pertaining to different symmetry types identically tend to zero (exact method of diagonalization).

The method of successive diagonalization as a mathematical procedure provides for the selection of coefficients of the linear transformation of coordinates under which the nondiagonal coefficients become, even if not equal to zero, then sufficiently small, that is, this is a method for the approximate solution of the secular equation.

Symmetry Reduction of F- and G-Matrices

Analysis of the symmetry properties of molecules is necessary in the interpretation of vibrational spectra. In the infrared spectrum and in the combination scattering spectrum of a molecule are manifested only the vibrations which are permitted by the

selection rules. The latter are determined by molecular symmetry. For example, in a polyatomic molecule that has a symmetry center i, vibrations that are symmetrical relative to i (g = "gerade" vibrations) are active in the combination scattering spectrum and inactive in the infrared spectrum and, conversely, vibrations that are antisymmetric relative to i (u = "ungerade" vibrations) are active in the infrared spectrum and inactive in the combination scattering spectrum.

To determine the vibrational frequencies, taking the symmetry properties into account is not generally speaking obligatory. Reducing the order of the secular equation, which can be achieved by reducing it by means of the symmetry coordinates to the quasi- /32
diagonal form, is not fundamentally important when modern computers (electronic computers) are used. However, in several cases, particularly when calculating highly symmetric molecules, symmetry reduction can so greatly simplify the solution of the vibrational problem, by reducing it to the solution of several algebraic levels of the first, second, and third order, that it no longer becomes necessary to use the computer. This in several cases can prove to be very useful.

Ordinarily, the **F** and **G** matrices are symmetry-reduced before being multiplied together. Mathematically, this operation involves a certain linear transformation of the equivalent coordinates, reducing each of the matrices to the quasidiagonal form.

Converting to new coordinates (in this case to symmetry coordinates) can be done by means of the similarity transformation with a certain matrix U:

$$\mathbf{F}' = \mathbf{UFU}; \tag{I.56}$$

$$\mathbf{G}' = \mathbf{UGU}. \tag{I.57}$$

This operation is analogous to the above-demonstrated transformation of the expression for the potential energy by employing the matrix **R** corresponding to the conversion from Cartesian coordinates to internal coordinates.

The question of whether in general it is possible to transform a matrix to the quasidiagonal form, and the methods of finding the coefficients of the matrix U are examined in group theory.

As noted above, symmetry operations characterizing a molecule form a set which corresponds to the mathematical concept of a group. A group is characterized by representations -- by a set

of numbers or analytic expressions which in one way or another are set up in accordance with the group elements. From this point of view, F- and G-matrices are different representations of the group to which the given molecule pertains.

The representations may be reducible and nonreducible. A reducible representation can always be decomposed into irreducible representations. If given representations have a matrical form, the irreducible representations of a given reducible representation actually will constitute the diagonal submatrices that are formed through the diagonalization of the matrix of the reducible representation. The number of irreducible representations into which a given reducible representation can be decomposed is equal to the number of classes which comprise the given group.

The membership of a molecule in a particular group (point group) is determined by the number and kind of symmetry operations characterizing it. For example, a molecule with only a second-order symmetry axis is in group C_2; if it has also a symmetry plane in which this axis lies, then this will be the C_{2v} group, and if the symmetry plane is perpendicular to the axis -- the group C_{2k}. If besides the principal axis, there are also n second-order axes perpendicular to it, the molecule belongs to the group D_h, and if further to it is added a symmetry plane, the group D_{nh} or D_{nd} is formed, and so on. /33

The number of classes for each point group in group theory is determined. For example, group T_d to which belongs, in particular, the methane molecule, has five classes: A_1, A_2, E, F_1, and F_2.

Thus, from group theory it follows that F- and G-matrices of any molecule exhibiting symmetry can be diagonalized, where the number of submatrices into which the matrices F and G can be decomposed is determined by the membership of the molecule in the particular point group. Since each symmetry coordinate describes in the given class the entire set of the given kind of equivalent internal coordinates, then obviously the order of the submatrix must not be higher than the order of the kinds of internal coordinates used to describe the vibrations of the given molecule. For example, the methane molecule is characterized only by two internal coordinates: q -- extension of the C-H bond, and α -- -- variation in the tetrahedral angle between the C-H bonds.

Therefore, the submatrices corresponding to the different classes of the group T_d will have an order not higher than the second, while the initial F- and G-matrices will be of the ninth

order. This means that when the symmetry properties are used, the vibrational problem for methane reduces to solving no more than five equations of no higher than the second order (virtually two first-order equations and one -- of the second order) instead of solving one ninth-order equation.

In group theory methods of constructing symmetry coefficients have been established /13/, that is, finding the elements of matrix **U** by means of which a transformation of the form of Eqs. (I.56) and (I.57) is carried out. These coefficients have been calculated and tabulated for several point groups /21/.

If the symmetry coefficients and the form of the matrix **U** are known, and thus, the transposed matrix $\tilde{U}$ is determinant, the problem boils down to multiplying the corresponding matrices together, as the result of which one must obtain quasidiagonal matrices **F'** and **G'**. In practice, however, the elements of the submatrices are sought for directly.

Obviously, for each class there will exist matrices of the following form in the symmetry coordinates S:

$$\mathbf{G}'_{A_1}=\begin{array}{c|ccc} & S_Q & S_q & S_\beta \\ \hline S_Q & \{G'\}_{QQ} & \{G'\}_{Qq} & \{G'\}_{Q\beta} \\ S_q & \{G'\}_{qQ} & \{G'\}_{qq} & \{G'\}_{q\beta} \\ S_\beta & \{G'\}_{\beta Q} & \{G'\}_{\beta q} & \{G'\}_{\beta\beta} \end{array} \quad \text{and} \quad \mathbf{F}'_{A_1}=\begin{array}{c|ccc} & S_Q & S_q & S_\beta \\ \hline S_Q & \{F'\}_{QQ} & \{F'\}_{Qq} & \{F'\}_{Q\beta} \\ S_q & \{F'\}_{qQ} & \{F'\}_{qq} & \{F'\}_{q\beta} \\ S_\beta & \{F'\}_{\beta Q} & \{F'\}_{\beta q} & \{F'\}_{\beta\beta} \end{array} \qquad \text{(I.58)}$$

Elements of the submatrices are determined from the following /34 formulas, expressing the coefficients of interaction of the symmetry coordinates in terms of the coefficients of the interaction of the natural coordinates /21/:

$$\{G\}'_{Qq}=\sum_j \{G\}_{Q_i q_i}\frac{\{U\}_{q_j}}{\{U\}_{Q_i}}; \qquad \text{(I.59)}$$

$$\{F\}'_{Qq}=\sum_j \{F\}_{Q_i q_i}\frac{\{U\}_{q_j}}{\{U\}_{Q_i}}, \qquad \text{(I.60)}$$

where Q and q are the kinds of equivalent coordinates; i and j are the numbers of the equivalent coordinates, where for a fixed i (we can take any j) all the numbers of a given kind of equivalent coordinates can be traversed.

Calculation of Roots and Finding of Frequencies

After finding symmetry-reduced matrices, for each isotopic species one sets up a set of secular equations of the form

$$\begin{aligned} &|\mathbf{G}'\mathbf{F}' - \mathbf{I}\lambda| = 0 \qquad |\mathbf{G}^{*\prime}\mathbf{F}' - \mathbf{I}\lambda^*| = 0 \\ &|\mathbf{G}''\mathbf{F}'' - \mathbf{I}\lambda| = 0 \qquad |\mathbf{G}^{*\prime\prime}\mathbf{F}'' - \mathbf{I}\lambda^*| = 0 \\ &\cdots\cdots\cdots\cdots \\ &\cdots\cdots\cdots\cdots \end{aligned} \tag{I.61}$$

The force constants of the molecule, the configuration and interatomic distances, that is, properties dependent on electronic structure, do not change in the conversion to the isotopically-replaced molecule. Therefore the F-matrix, when the vibrational problem is solved for the isotopically replaced species, remains unchanged. The structure of the elements of the G-matrix also remains unchanged. Only the values of the mass of atoms appearing in the G-matrix change.

When there is complete isotopic replacement, the molecular symmetry is preserved. In the case of a partially replaced isotopic species, one must deal with the disruption (reduction) of molecular symmetry. In particular, this leads to the cleavage of vibrations and removal of degeneracy in the case of highly symmetric molecules.

The number of equations is equal to the number of classes. Since mass appears only in the expression for the coefficients $\{G\}_{ij}$, and the force constants do not depend on mass, only the elements $\{G\}^*_{ij}$, are found for the isotopic species, while the F-matrix is general.

If the problem is solved without a computer, each secular equation is expanded into an algebraic equation of the corresponding order: /35

$$\lambda^n - c_1\lambda^{n-1} - c_2\lambda^{n-2} - \ldots - c_{n-1}\lambda - c_n = 0. \tag{I.62}$$

The coefficients of this polynomial can be found by expanding the matrix

$$\begin{vmatrix} \{GF\}_{11} - \lambda & \{GF\}_{12} & \{GF\}_{13} \ldots \\ \{GF\}_{21} & \{GF\}_{22} - \lambda & \{GF\}_{23} \ldots \\ \{GF\}_{31} & \{GF\}_{32} & \{GF\}_{33} - \lambda \ldots \\ \cdot & \cdot & \cdot \quad \cdot \\ \cdot & \cdot & \cdot \quad \cdot \end{vmatrix} = 0$$

through the successive computation of the minors. When the matrices of high orders (above the third) are expanded, it is more convenient to use the Frahm method of finding the coefficients of the polynomial:

$$c_1 = \text{Spur}\,\mathbf{GF}, \tag{I.63}$$

where Spur or "trace" is the sum of the diagonal elements of the matrix;

$$c_2 = \text{Spur}\,[(\mathbf{GF})(\mathbf{GF})_1/2];$$
$$(\mathbf{GF})_1 = (\mathbf{GF}) - \mathbf{I}c_1. \tag{I.64}$$

In general, the k-th coefficient c_k is determined by the formula

$$c_k = \text{Spur}\,[(\mathbf{GF})(\mathbf{GF})_{k-1}/k];$$
$$(\mathbf{GF})_{k-1} = (\mathbf{GF})(\mathbf{GF})_{k-2} - \mathbf{I}c_{k-1}. \tag{I.65}$$

After finding all the coefficients of the polynomial, the equations are solved for λ and λ^*. Next, one determines the frequencies ν and ν^* and computes the ratio of the distribution functions over state or β-factor.

In the numerical solution of the secular equation, one must take note of the dimensions of the quantities appearing in the secular equation. The elements of the G-matrices are obtained dimensionless when the relative quantities $\mu_C = \frac{m_H}{m_C}$ and $\sigma_C = \frac{r_{CH}}{r_{CC}}$ are used, or if $\mu_C = \frac{1}{m_C}$, then the elements of the G-matrices have the dimension of atomic unit of mass /a.u.m/. The force constants can be expressed in the units of 10^5 dynes/cm (or mdynes/AU). In this case the wave number $\tilde{\nu}$ (or the frequency in reciprocal centimeters) is $\tilde{\nu} = \sqrt{\lambda}/2\pi c$ (the dimensionality is determined by the ratio $\tilde{\nu} = \sqrt{f/\mu}/2\pi c$): $\tilde{\nu}\ (\text{cm}^{-1}) = 1303.16\sqrt{\lambda}$. If the force constants are expressed in the units 10^6 cm^{-2}, then $\tilde{\nu}$ is obtained at once as the square-root from λ: $\tilde{\nu}\ (\text{cm}^{-1}) = \sqrt{\lambda}$.

Methods of Verifying the Correctness of the Solution to the Vibrational Problem /36

The main method of verifying the correctness of the solution to the vibrational problem, in particular, the correctness of the

choice of the values of the force constants, the correctness of the coordinate analysis, and so on, is to compare the frequencies obtained by calculation with those experimentally observed.

Included among the methods of verifying the correctness of the mathematical solution of the problem, that is, finding the roots of the secular equation, are the following:

a) when solving the equation without eliminating superfluous coordinates, zero roots must be obtained;

b) the sum of the diagonal coefficients of the secular equation is equal to the sum of the roots:

$$\sum_{i}^{n} \lambda_i = \text{Spur } \mathbf{GF}; \tag{I.66}$$

c) the product of the roots of the secular equation is equal to the determinant of **GF**:

$$\prod_{i}^{n} \lambda = \text{Det } \mathbf{GF}. \tag{I.67}$$

Computer Calculations

By setting up the **F**- and **G**-matrices of the molecule under study, one can carry out further operations in multiplying the matrices together and finding their eigenvalues (roots) with an electronic computer, using standard mathematical programming. However, there are specialized programs for the machine solution of the vibrational problem, where they provide not only for operations on matrices, but also for setting up the matrices as such, in particular, the kinematic coefficients of the **G**-matrix, which is quite difficult to do manually.

We calculated the isotopic frequencies of organic compounds on a Minsk-22 electronic computer, by using a program developed by L. A. Gribov et al. [5, 10]. By this program, the computer itself sets up the **G**-matrix. Here as the initial information, the values of the direction cosines of the vectors of the interatomic bonds are given in a Cartesian coordinate system, the inverse bond length in AU^{-1} $\{\sigma\}$, the inverse masses $\{\varepsilon\}$ relative to the spectroscopic mass of hydrogen, and the set of internal coordinates.

The symmetry matrix **U** is set up in advance, for example, by the method of symmetry vectors /5/, and its elements, row by row, are punched into the input information tape. The **F**-matrix is set up on the basis of a selected system of force constants and is fed into the electronic computer in triangular form.

By this, the preparation and input of the initial information /37 is at an end. Further operations are carried out by the machine following a program that provides for converting from the natural vibrational coordinates to the symmetry coordinates and determining the roots by the method of successive diagonalization. Besides the vibrational frequencies, at the output are furnished the shape factors of the vibrations, by which the assignment of the resulting frequencies is carried out.

The calculation boils down to achieving the best agreement of the calculated and experimental frequencies. If the agreement is unsatisfactory, the force constants are corrected. The instruction to the program makes it possible to introduce from a specific address a variant of the **F**-matrix and to obtain a new set of frequencies. The force coefficients are corrected either by using the solution of the inverse spectral problem, or else by the successive selection of force constants.

If a set of frequencies is obtained coinciding with a known vibrational spectrum of a molecule (the values of the experimentally observed frequencies are taken from a listing by L. I. Sverdlov et al.) /10/, one begins calculating the isotopic frequencies. This is achieved by the appropriate variation in the initial values of the matrix of the inverse masses $\{\varepsilon\}$. The cycle of computations is repeated for all independent isotopically-replaced species of the given compound.

The program for calculating the isotopic frequencies has been combined in the variant we used with the program for calculating β-factors, drawn up on request of our laboratory by staff members of the physics department at the Timiryazevskaya Agricultural Academy (by V. A. Dement'yev et al.) under the supervision of L. A. Gribov. After the solution of the vibrational problem and the printout of the isotopic frequencies into the operational memory of the computer, the program for calculating the β-factors is engaged and they are computed successively for specified temperatures. In most cases, the calculation is carried out in the 100-1500° K temperature range for every 50° K. In the next section are given the isotopic frequencies and β-factors of calculated compounds, as well as brief initial data. More detailed information is given in another study /4/.

Thermodynamic Isotopic Factors of Carbon Compounds

The isotopic constants of hydrocarbons were calculated in our laboratory as part of the program of studying the isotopic composition of carbon in natural hydrocarbons.

As a result, thermodynamic isotopic factors of CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, benzene, toluene, and cyclohexane were calculated, that is, representatives of all classes of petroleum hydrocarbons were investigated: paraffinic, aromatic, and naphthenic. In addition, since in discussing the genetical relationships of petroleum hydrocarbons with the biochemical constituents of organic matter, and also in interpreting the isotopic composition of tars, asphaltenes, and so on, it is important to know the effect on the isotopic composition of the carbon in heteroatomic substituents, so the thermodynamic isotopic factors were calculated for a series of typical heteroatomic organic compounds -- acetic acid (CH_3COOH), methanol (CH_3OH), acetaldehyde (CH_3CHO), and methylamine (CH_3NH_2). /38

Paraffinic Hydrocarbons

Methane CH_4

Geometry. The configuration is tetrahedral (Fig. 2). The distance between the carbon atom and the hydrogen atoms r_{C-H} = = 1.09 AU; the angles $\mathbf{H{-}C{-}H}$ between the bonds are equal to each other and are equal to the tetrahedral value -- 109°28'.

Force constants (in units of 10^6 cm^{-2}). f_q = 8.340, f_α = = 0.710, f_{qq} = 0.50, $f_{q\alpha}$ = 0.350, and $f_{\alpha\alpha}$ = -0.035 [21]. The subscripts in the force constants correspond to the internal coordinates whose interaction is being described. The physical significance of the notation of the coordinates is clear from Fig. 2. This set of force constants was used in calculating isotopic frequencies in [42]. /39

Symmetry and classes of vibrations. Point group T_d. Irreducible representation: $\Gamma = A_1 + E_1 + 2F_2$ (the letter indices denote the vibration classes, while the numbers in front of them denote the order of the corresponding equations). Vibrations pertaining to class E are twice-degenerate, and those pertaining to class F are thrice-degenerate. As a result, from 3N - 6 = 9 frequencies of methane, four are observed in the spectrum (Table 2).

TABLE 2. VIBRATIONAL FREQUENCIES AND ISOTOPIC FREQUENCY SHIFTS OF METHANE AND ETHANE

Methane				Ethane			
Vibr. class	Obs., cm^{-1} ν_i	Calculated ν, cm^{-1}	Calculated $\Delta\nu$, cm^{-1}	Vibr. class	Obs., cm^{-1} ν_i	Calculated ν, cm^{-1}	Calculated $\Delta\nu$, cm^{-1}
A	2914	2914.1	0	A_g	995	997.6	30.0
E	1533	1533.7	0		~2925	2902.0	3.4
F	3022	3015.9	10.9		1375	1380.6	11.5
	1304	1304.0	9.1	A_u	2895	2897.1	2.7
					1380	1379.9	10.1
				E_g	2960	2970.4	10.3
					1170	1177.5	16.5
					1458	1457.9	0.3
				E_u	2980	2984.1	10.9
					827	834.1	2.1
					1465	1468.3	3.2

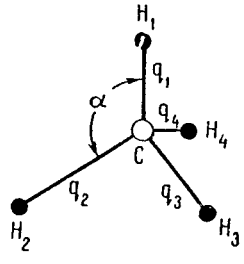


Fig. 2. Methane molecule

β-factors. The monoatomic methane molecule is characterized by a single value of the β-factor (see Table 2).

Ethane C_2H_6

Geometry. The configuration is "chessboard" (Fig. 3). The distance between the carbon atoms (bond length) $r_{C-C} = 1.55$ AU; $r_{C-H} = 1.09$ AU; the angles between the C-H and the angles between the C-C bonds are equal to each other and are approximately equal to the tetrahedral value -- -- $109^{\circ}28'$.

Force constants.(in units of 10^6 cm^{-2}). $f_Q = 7.020$, $f_{Qq} = 0.050$, $f_{Q\beta} = 0.435$, $f_q = 8.065$, f_{qq} (type $f_{q_1q_2} = 0.050$, $f_{q_1q_4} = 0$), $f_{q\beta}$ ($f_{q_1\beta_1} = 0.350$, type $f_{q_1\beta_2} = 0$), $f_{q\alpha}$ ($f_{q_1\alpha_{31}} = 0.350$, $f_{q_1\alpha_{23}} = 0$), $f_\beta = 0.920$, $f_{\beta\beta}$ (type $f_{\beta_1\beta_2} = -0.035$, $f_{\beta_1\beta_4} = 0.120$, $f_{\beta_1\beta_6} = -0.020$), $f_\alpha = 0.710$, $f_{\alpha\beta}$ (type $f_{\alpha_{23}\beta_2} = 0$, $f_{\alpha_{23}\beta_2} = 0.035$),

and $f_{\alpha\alpha}$ (type $f_{\alpha_{23}\alpha_{31}} = -0.035$, $f_{\alpha_{23}\alpha_{45}} = 0$). The force constants f_α, f_{qq}, $f_{q\alpha}$, and $f_{\alpha\alpha}$ are taken equal to the corresponding force constants of methane.

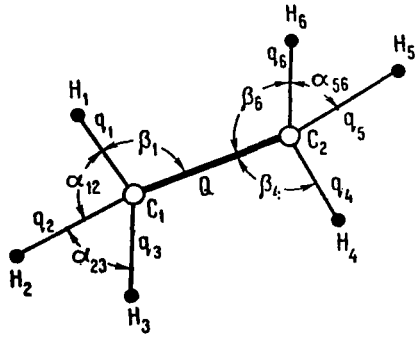


Fig. 3. Ethane molecule

Symmetry and classes of vibrations. Point group D_{3d}. Irreducible representation: $\Gamma = 3A_g + 2A_u + 3E_g + 3E_u$. The frequencies pertaining to classes E_g and E_u are twice-degenerate. Of the 3N - 6 = 18 frequencies of ethane /42/, 17 have been determined. The frequency corresponding to twisting of the C-C bond was not taken into account in calculating the β-factor.

β-factors. Ethane contains two equivalent atoms, therefore it is characterized by a single value of the β-factor (Table 4). /40

Propane C_3H_8

Geometry. The configuration is shown in Fig. 4. The distance between the atoms $r_{C-C} = 1.54$ AU, and $r_{C-H} = 1.09$ AU; all the angles between the bonds, including the angle $\overset{\diagup\diagdown}{C-C-C}$, are approximately equal to the tetrahedral value: $\alpha = \beta = \gamma = 109°28'$.

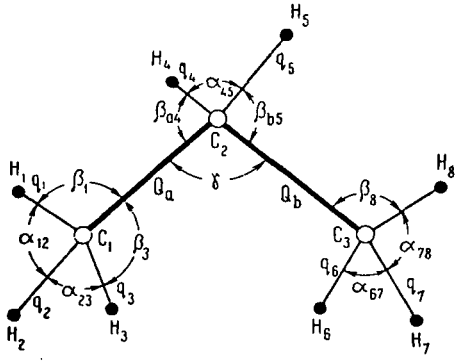


Fig. 4. Propane molecule

Force constants. f_q (type $f_{q_4} = 7.890$, and the rest are $f_q = 8.065$), $f_\gamma = 1.100$, $f_{\gamma\beta}$ (type $f_{\gamma\beta_2} = 0.120$, $f_{\gamma\beta_1} = -0.020$). The force constants characterizing the interaction of the remaining coordinates are assumed to be equal to the corresponding force constants for ethane. /41

Symmetry and vibration classes. Point group C_{2v}. Irreducible representation: $\Gamma = 9A_1 + 4A_2 + 5B_1 + 7B_2$.

TABLE 3. VIBRATIONAL FREQUENCIES AND ISOTOPIC FREQUENCY SHIFTS FOR PROPANE

Vibration class	Frequency number	Observed ν, cm^{-1}	Calculated ν, cm^{-1}	Calculated $\Delta\nu$, cm^{-1} $(C-C^{13}-C)$	Calculated $\Delta\nu$, cm^{-1} $(C^{13}-C-C^{13})$
A_1	1	373	349.6	2.5	5.7
	2	2973	2978.7	0	10.7
	3	2890	2899.9	5.7	0
	4	2875	2883.5	2.5	1.3
	5	1487	1471.6	0	10.7
	6	1372	1380.1	2.1	0.2
	7	1452	1440.4	10.9	11.2
	8	1145	1139.0	6.0	15.7
	9	867	865.9	0	10.6
A_2	10	2968	2977.4	0	10.6
	11	1452	1452.7	0	0.6
	12	923	929.3	0	4.3
	13	1278	1294.1	0	5.5
B_1	14	2973	2973.3	0.5	10.1
	15	2922	2931.5	10.6	0.5
	16	1468	1467.1	0.8	1.2
	17	1165	1170.7	9.8	9.7
	18	747	717.0	2.7	0.2
B_2	19	1064	1072.0	11.1	11.4
	20	2969	2976.2	0	10.4
	21	2890	2899.6	0	3.0
	22	1468	1469.5	2.0	1.1
	23	1390	1380.7	0.2	11.2
	24	923	939.6	1.9	7.3
	25	1355	1353.1	16.5	3.4

TABLE 4. THERMODYNAMIC ISOTOPIC FACTORS OF METHANE, ETHANE, AND PROPANE AT DIFFERENT TEMPERATURES

T, K	Methane $\beta_i = \beta_\Sigma$	Ethane $\beta_i = \beta_\Sigma$	Propane β_i $(C-C^{13}-C)$	Propane β_i $(C^{13}-C-C^{13})$	Propane β_Σ
100	1.4682	1.5967	1.7282	1.6159	1.6530
200	1.1931	1.2333	1.2706	1.2364	1.2478
300	1.1136	1.1317	1.1493	1.1331	1.1385
400	1.0765	1.0861	1.0956	1.0867	1.0895
500	1.0554	1.0610	1.0666	1.0613	1.0680
600	1.0421	1.0455	1.0491	1.0457	1.0468
700	1.0331	1.0353	1.0376	1.0354	1.0361
800	1.0267	1.0282	1.0298	1.0283	1.0288
900	1.0220	1.0229	1.0241	1.0230	1.0233
1000	1.0184	1.0191	1.0199	1.0191	1.0193
1100	1.0156	1.0161	1.0167	1.0161	1.0163
1200	1.0134	1.0138	1.0142	1.0138	1.0139
1300	1.0115	1.0119	1.0122	1.0119	1.0120
1400	1.0101	1.0104	1.0106	1.0104	1.0105
1500	1.0089	1.0091	1.0093	1.0091	1.0091

No degenerate vibrations. Twenty five of 3N - 6 = 27 isotopic frequencies were calculated. Two frequencies corresponding to twisting of the C-C bond were not taken into account (see Table 3).

β-factors. Propane has two groups of equivalent atoms, and, therefore, is described by two β_i-factors, one of which characterizes isotopic replacement at the central atom (CH_2 group), and the other -- at a peripheral atom (CH_3 group). The value of β_Σ is /42 is determined in accordance with Eq. (I.32). Its values are given in Table 4 for different temperatures.

Butane C_4H_{10}

Geometry. Molecules of normal paraffinic hydrocarbons with the atoms numbering more than three have an extended configuration, forming a plane zigzag chain of carbon atoms. The end CH_3 groups are tetrahedral in structure, where on hydrogen atom lies in the plane of the carbon skeleton, while the remaining hydrogen atoms of the CH_3 groups and the CH_2 groups form pairs symmetrical with respect to this plane. Fig. 5 shows the structure of a pentane molecule, whose configuration and parameters, with the exception of a single CH_2 group, also characterize the butane molecule.

Force constants. $f_{\gamma\gamma} = 0.12 \cdot 10^6$ cm^{-2}, and the remaining are transferred without change from methane and propane.

Symmetry and vibration classes. Point group is C_{2h}. Irreducible representation: $\Gamma = 11A_g + 8A_u + 7B_g + 10B_u$. Of the 36 vibrational frequencies corresponding to 3N - 6 vibrational degrees of freedom of butane /42/, 33 have been calculated (Table 5). Two frequencies belonging to class A_u, and one frequency belonging to class B_g drop out, since twisting of the C-C bonds was not taken into account.

β-factors. A model of normal butane has two groups of equivalent covered atoms: two central and two peripheral. In accordance with this situation, the vibrational problem was solved, in addition to the main, also for two isotopic species of butane. Two values of the β_i-factors were obtained and the β_Σ-factor was calculated (see Table 7).

TABLE 5. VIBRATIONAL FREQUENCIES AND ISOTOPIC FREQUENCY SHIFTS FOR BUTANE

/43

Vibration class	Frequency number	Observed [38] ν, cm^{-1}	Calculated $\Delta\nu$, cm^{-1} ($C-C^{13}-C^{13}-C$)	Calculated $\Delta\nu$, cm^{-1} ($C^{13}-C-C-C^{13}$)	Calculated ν, cm^{-1}
A_g	1	1057	15.2	9.6	1066.8
	2	426	3.4	7.9	395.7
	3	2965	0	10.6	2977.5
	4	2877	0.1	3.0	2899.7
	5	2860	6.0	0	2883.4
	6	837	12.2	5.8	840.2
	7	1460	3.6	1.1	1473.8
	8	1444	2.4	0	1436.9
	10	1382	8.3	9.5	1378.9
	11	1361	13.8	3.1	1387.2
A_u	12	2976	0.4	10.3	2978.6
	13	2927	11.0	0.4	2938.6
	14	1454	0.3	1.3	1463.2
	15	958	1.4	4.3	981.8
	16	1260	3.3	4.4	1276.5
	17	733	2.4	0	675.2
B_g	18	2962	0.2	10.4	2978.2
	19	2914	10.5	0.2	2925.4
	20	1460	0.5	1.4	1463.9
	21	1168	13.1	7.5	1163.6
	22	809	3.8	0.9	804.3
	23	1301	1.7	1.2	1308.7
B_u	24	1010	16.8	14.8	1018.4
	25	2967	0	10.0	2977.4
	26	2878	0.2	3.0	2899.9
	27	2860	5.6	0	2884.4
	28	222	3.6	2.5	249.2
	29	1480	2.5	1.2	1470.3
	30	1467	3.2	0.3	1451.0
	31	967	0.3	8.4	993.3
	32	1380	0	10.9	1380.3
	33	1300	11.4	3.1	1299.7

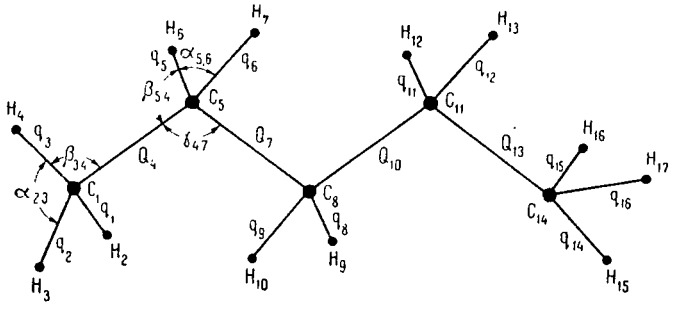


Fig. 5. Pentane molecule

TABLE 6. VIBRATIONAL FREQUENCIES AND ISOTOPIC FREQUENCY SHIFTS FOR PENTANE /44

Vibr. class	Freq. nr.	Obs. ν, cm^{-1}	Calculated ν cm^{-1}	$\Delta\nu$, cm^{-1} ($C-C-C^{13}-C-C$)	$\Delta\nu$, cm^{-1} ($C-C^{13}-C-C^{13}-C$)	$\Delta\nu$, cm^{-1} ($C^{13}-C-C-C-C^{13}$)
A_1	1	2973	2977.5	0	0	10.6
	2	1033	1054.3	1.0	16.4	11.2
	3	179	172.0	12.6	8.3	24.4
	4	2866	2855.1	0.9	7.0	0.1
	5	2892	2899.8	0	0	3.0
	6	2866	2883.4	5.1	0	0
	7	1480	1460.9	0.3	2.2	1.3
	8	863	880.1	8.0	5.5	3.5
	9	1142	1138.1	8.9	12.6	5.1
	10	1379	1357.3	0	0.4	10.9
	11	1346	1338.8	0.3	15.6	1.6
	12	1442	1421.8	0	2.9	0.3
	13	401	367.4	0.9	3.9	6.6
	14	1463	1453.1	4.0	0.7	0.4
A_2	15	2967	2978.4	0	0.3	10.3
	16	2908	2932.7	0	10.8	0.3
	17	1462	1463.7	0	0.4	1.3
	18	993	1012.4	0	2.5	4.0
	19	1303	1309.8	0	1.9	0.2
	20	766	739.4	0	3.7	0.1
	21	1269	1256.3	0	4.8	5.3
B_1	22	2967	2978.4	0.1	0.3	10.3
	23	2930	2943.1	4.6	3.9	0.2
	24	2930	2922.9	6.5	6.9	0.1
	25	1469	1463.4	0	0.4	1.4
	26	856	866.9	3.5	1.0	1.6
	27	1170	1159.9	4.8	10.6	5.9
	28	1303	1306.9	4.0	0	2.1
	29	727	656.9	1.0	1.0	0
B_2	30	2967	2977.5	0	0	10.6
	31	406	380.0	1.7	4.4	2.0
	32	1073	1087.1	8.7	8.4	1.3
	33	2879	2899.8	0.0	0.1	3.0
	34	2866	2883.8	0	5.8	0
	35	1476	1466.1	1.5	4.3	1.2
	36	910	934.0	7.2	6.1	9.5
	37	1021	1035.3	0	8.8	10.4
	38	1379	1356.5	0.2	0.1	10.3
	39	1269	1272.8	4.3	5.6	2.4
	40	1389	1387.3	9.0	10.6	0.7
	41	1456	1436.0	1.6	4.2	0.8

Pentane C_5H_{12} /45

Geometry. The configuration of the molecule is shown in Fig. 5. Parameters: r_{C-C} = 1.54 AU, r_{C-H} = 1.09 AU, and the angles $\widehat{H-C-H}$, $\widehat{HCC}$, $\widehat{CCC}$ are equal to each other and are are equal to the tetrahedral value -- 109°28'.

Force constants. The same system as for butane.

Symmetry and vibration classes. Point group C_{2u}. Irreducible representation: $\Gamma = 4A_1 + 9A_2 + 12B_1 + 10B_2$. Forty-one frequencies out of 45 were calculated (Table 6); four frequencies ($2A_2$ and $2B_1$) are absent for the same reason as for butane.

β-factor. The pentane molecule has three groups of equivalent carbon atoms: two carbon atoms of the CH_3 groups, two carbon atoms of the CH_2 groups in the α-position, and one central carbon atom. Accordingly, with the computer the values of three β_i-factors were calculated, and under Eq. (I.32), the β_Σ-factors were calculated (Table 7).

TABLE 7. THERMODYNAMIC ISOTOPIC FACTORS FOR THE CARBON IN n-BUTANE AND n-PENTANE

	n-Butane			n-Pentane			
	β_i-factor			β_i- factor			
T, K	$C-C^{13}-C^{13}-C$	$C^{13}-C-C-C^{13}$	β_Σ factor	$C-C-C^{13}-C-C$	$C-C^{13}-C-C^{13}-C$	$C^{13}-C-C-C-C^{13}$	β_Σ- factor
100	1.7431	1.6194	1.6810	1.7553	1.7452	1.6198	1.6971
200	1.2741	1.2366	1.2553	1.2771	1.2741	1.2365	1.2597
300	1.1531	1.1531	1.1419	1.1519	1.1506	1.1330	1.1450
400	1.0963	1.0867	1.0915	1.0969	1.0963	1.0866	1.0925
500	1.0670	1.0613	1.0641	1.0674	1.0670	1.0613	1.0648
600	1.0493	1.0457	1.0475	1.0496	1.0493	1.0457	1.0479
700	1.0378	1.0354	1.0366	1.0380	1.0378	1.0354	1.0369
800	1.0399	1.0283	1.0291	1.0300	1.0299	1.0282	1.0292
900	1.0242	1.0230	1.0236	1.0243	1.0242	1.0230	1.0237
1000	1.019	1.0191	1.0195	1.0200	1.0199	1.0191	1.0196
1100	1.0167	1.0161	1.0164	1.0168	1.0167	1.0161	1.0165
1200	1.0142	1.0138	1.0140	1.0143	1.0142	1.0138	1.0141
1300	1.0122	1.0119	1.0121	1.0123	1.0123	1.0119	1.0122
1400	1.0107	1.0104	1.0106	1.0107	1.0107	1.0104	1.0106
1500	1.0093	1.0091	1.0092	1.0094	1.0093	1.0091	1.0092

Correlation Formula for High-Molecular Paraffinic Hydrocarbons /46

If one writes out the β-factors of the isotopic species for any particular temperature, for example, 300° K (Table 8), then it is clear that adding a new carbon atom to the homologous series

does not change the β-factors characterizing replacement at the preceding atoms. And the β-factor corresponding to the newly added atom differs even less from the preceding atom and tends to some limiting value.

This correlation affords grounds for extrapolation: the β_Σ-factors of hydrocarbons of the normal alkane series are described by the following correlation formula (at 300° K):

$$\beta_{\Sigma\, C_nH_{2n+2}} = \frac{1}{2}\,[4{,}5672 + 1{,}1520\,(n-4)]. \qquad (I.68)$$

Comparing the thermodynamic isotopic factors calculated by Eq. (I.68) with those obtained by direct quantum-statistical calculation shows their nearly total agreement (Table 9).

TABLE 8. β-FACTORS OF NORMAL ALKANES (300° K)

Molecule	C^{13}	$C-C^{13}$	$C-C-C^{13}$
C_2H_6	1,13169	—	—
C_3H_8	1,13305	1,14934	—
C_4H_{10}	1,13305	1,15066	—
C_5H_{12}	1,13300	1,15064	1,15193

TABLE 9. THERMODYNAMIC ISOTOPIC FACTORS OBTAINED BY DIRECT CALCULATION AND BY CORRELATION FORMULA (I.68) (300° K)

Molecule	Direct calculation (Table 7)	Calculation by correlation Eq. (I.68)
C_2H_6	1,13169	1,1316
C_3H_8	1,13848	1,1384
C_4H_{10}	1,14185	1,1418
C_5H_{12}	1,14384	1,1438
C_6H_{14}	—	1,1452
C_7H_{16}	—	1,1462

Thus, using the additive properties of the β-factors of a homologous series, without resorting to solving the vibrational problem we can obtain the β_Σ-factors of hexane, heptane, octane, and so on for the entire series of normal alkanes. /47

TABLE 10. TEMPERATURE COEFFICIENTS FOR THE FORMULA USED IN DETERMINING β-FACTORS AND α IN THE NORMAL ALKANE SYSTEM /47

T, K	a_T	b_T	T, K	a_T	b_T
200	5.0206	1.2780	900	4.0944	1.0245
300	4.5672	1.1520	1000	4.0780	1.0200
400	4.3660	1.0970	1100	4.0656	1.0170
500	4.2564	1.0615	1200	4.0560	1.0145
600	4.1900	1.0495	1300	4.0484	1.0125
700	4.1464	1.0375	1400	4.0420	1.0107
800	4.1162	1.0300	1500	4.0368	1.0091

The partition coefficient of carbon isotopes between any components of a hydrocarbon system can be calculated by the formula

$$\alpha = \frac{m[a_T + b_T(n-4)]}{n[a_T + b_T(m-4)]}, \qquad (I.69)$$

which is a generalized formula for the notation of the ratios of the β-factors of the form (I.33). Here a_T and b_T are coefficients dependent on temperature; they were calculated by us for temperatures from 200 to 1500° K (Table 10).

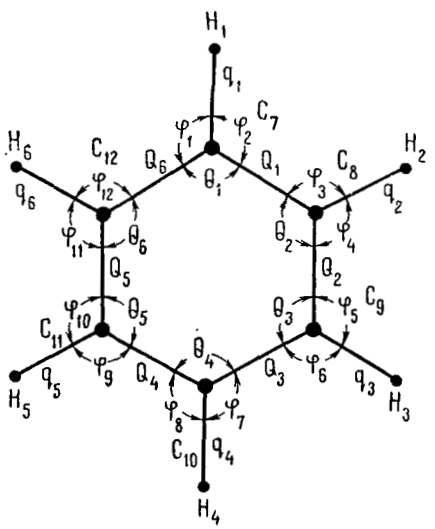


Fig. 6. Benzene molecule

Aromatic Hydrocarbons

Benzenes C_6H_6

Geometry. Configuration is planar (Fig.6). Parameters: r_{C-C} = 1.39 AU, r_{C-H} = 1.084 AU, and the angles $\widehat{CCH}$ and $\widehat{CCC}$ are equal to each other and are 120°.

Force constants. In describing the plane vibrations, use was made of the force field proposed by D. Duinker I. Mills /146/, and for the nonplane vibrations -- the field proposed by O'Reilly /204/. In view of the π-electron conjugation in the benzene /48

ring, the substantial interaction of spatially remote coordinates is provided for (in contrast to paraffinic hydrocarbons). A. A. Ivlev, in calculating, corrected the force constants and obtained a good agreement between the experimental and calculated frequencies. The total system of the force constants is cumbersome and is not presented here. One can refer to our study /[4]27/.

TABLE 11. VIBRATIONAL FREQUENCIES OF ISOTOPIC SPECIES OF BENZENE

Vibration class	Observed [146, 204] ν, cm^{-1}	Calculated ν, cm^{-1}	
		$C_6^{12}H_6$	$C_6^{13}H_6$
	Plane vibrations		
A_{1g}	993 3073	984 3073	949 3060
A_{2g}	1350	1361	1349
B_{1u}	3057 1010	3057 1000	3045 964
B_{2u}	1309 1146	1304 1167	1255 1164
E_g	3056 1599 1178 606	3056 1604 1181 611	3045 1544 1180 589
E_u	3064 1482 1037	3064 1471 1033	3053 1446 1011
	Extraplane vibrations		
A_{1u}	673	673	671
B	990 707	990 707	981 686
E	845	845	833
E	967 398	967 398	955 386

Symmetry and vibration classes. Point group is D_{6h}. Irreducible representation: $\Gamma = 3A_g + 2A_{2g} + 2B_{1u} + 4E_g + 3E_{1u} + A_{1u} + A_{2u} + B_{2g} + E_{1g} + E_{2u}$. Benzene atoms execute 3N - 6 = 30 vibrations, of which 2N - 3 = 21 vibrations are in the plane of the ring and N - 3 = 9 vibrations are outside the plane. The plane vibrations /49

are determined by 30 internal coordinates, whose physical significance is clear from Fig. 6. The extraplane vibrations are described by coordinates characterizing the projection of the C-H bond from the plane of the ring (γ), and by the coordinates of the twisting of C-C bonds with respect to the intermediate value. Isotopic frequencies corresponding to all molecular vibrations are shown in Table 11.

β-factors. All six carbon atoms of benzene are equivalent, therefore benzene is characterized by a single value of the β-factor (see Table 13).

Toluene C_7H_8

Geometry. The configuration of the toluene molecule is shown in Fig. 7. The length of the C-C and C-H bonds in the ring are equal to 1.39 AU and 1.084 AU -- just as in benzene. The length of the C-H bonds in the methyl group are taken as, as in ethane, 1.091 AU, and the C-C bonds between the methyl group and the ring -- -- as 1.54 AU. The angles $\theta_i = \phi_i = 120^\circ$, $\alpha_i = \beta_i = 109^\circ 28$. There are several rotary isomers of toluene, determined by the position of the CH_3 group relative to the plane of the ring. However, we know that the position of the CH_3 group has practically no effect on the spectrum /103/. In this view, the CH_3 group is turned so that one of the C-H bonds lies in the plane perpendicular to the plane of the ring. Here the molecule acquires symmetry with respect to this plane, which determines its membership in point group C_s.

Force constants. The force fields of the ring and the methyl group are segregated and interact weakly. This provides the prerequisite for approximating the force field of the toluene ring by the benzene field, and the force field of the CH_3 group of toluene -- by the field of the methyl group of alkanes. Only one new force constant is introduced, characterizing the interaction of the angles C-C-C which are external with respect to the ring. The force constant describing the rotation of the CH_3 group relative to the ring was not taken into account, since we do not know the corresponding experimental frequency. The system of the force constants we used is given in /42/. /51

Symmetry and vibration classes. Point group is C_s. Irreducible representation: $\Gamma = 22A' + 17A''$. Even with symmetry reduction, a 22nd-order equation has to be solved. The plane and extraplane vibrational frequencies of both classes are given in Table 12.

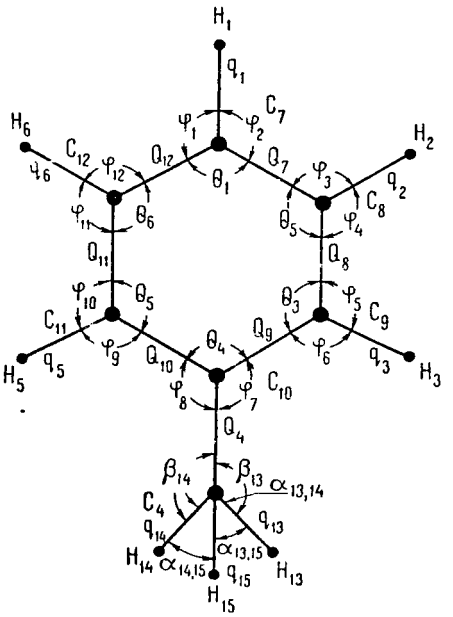


Fig. 7. Toluene molecule

β-factors. The addition of a methyl radical to the aromatic ring leads to a disruption of the structural equivalents of the ring atoms. As a result, five groups of nonequivalent atoms appear, therefore the vibrational problem has been solved for five differently substituted (in addition to the basic) isotopic species of toluene. As a result, five β_i-factors characterizing replacements by the following atoms were obtained:

$C_4 - \beta_I$; $C_7 - \beta_{II}$; $C_{10} - \beta_{III}$; C_8 and $C_{12} - \beta_{IV}$; C_9 and $C_{11} - \beta_V$ (Table 13).

Naphthenic Hydrocarbons -- /52

Cyclohexane C_6H_{12}

Geometry. Two rotary isomers of cyclohexane are known. One has the chair configuration, and the second the boat configuration. The second isomer at room temperature is present in vanishingly small amounts. Fig. 8 shows the configuration of the cyclohexane molecule in the chair form. Four carbon atoms lie in the same plane, and two others lie to both sides of it. Of the twelve C-H bonds, six are axial, and four are equatorial. The C-H bonds of the neighboring methylene groups lie in chessboard order. The parameters are: $r_{C-C} = 1.54$ AU, $r_{C-H} = 1.09$ AU, $\alpha_i = \beta_i = \gamma_i = 109°28'$.

Force constants (in units of 10^6 cm^{-2}). $f_q = 7.89$, f_{qq} (type $f_{q_1q_2} = 0.05$, $f_{q_1q_4} = 0.05$, $f_{q_1q_3} = 0.04$); $f_Q = 7.02$, $f_{QQ} = 0$, $f_{q\alpha} = 0.350$; $f_{q\beta} = 0.350$; $f_{Q\beta} = 0.435$; $f_{Q\gamma} = 0.435$, $f_\alpha = 0.710$, $f_\beta = 0.920$, $f_{\beta\beta}$ (type $f_{\beta_{7,6}\beta_{7,2}} = -0.035$, $f_{\beta_{7,6}\beta_{17,1}} = 0.12$, $f_{\beta_{7,6}\beta_{18,1}} = -0.02$), $f_\gamma = 1.4$, $f_{\beta\gamma}$ (type $f_{\beta_{7,6}\gamma_{2,6}} = -0.1$, $f_{\beta_{7,6}\gamma_{5,1}} = -0.02$); $f_{\gamma\gamma} = 0.2$. This system of force constants was used by us in calculating the isotopic frequencies /42/.

Symmetry and vibration classes. The point group is D_{3d}. Irreducible representation: $\Gamma = 6A_{1g} + 3A_{1u} + 2A_{2g} + 5A_{2u} + 8E_g + 8E_u$. Of the molecules we calculated, the highest polyatomic molecule cyclohexane has 3N - 9 = 48 vibrational frequencies, of which 16 belonging in classes E_g and E_u are twice-degenerate. All 32 values of the cyclohexane frequencies are given in Table 14.

TABLE 12. VIBRATIONAL FREQUENCIES OF ISOTOPIC SPECIES OF TOLUENE /50

Vibration class	Obs. ν, cm^{-1}	Calculated frequencies of nonequivalent isotopic species of toluene ν, cm^{-1}					
		Basic form $C_6H_5CH_3$	Isotopically-replaced species (number of replaced atoms from Fig. 7)				
			C_{10}	C_4	C_7	$C_{8,12}$	$C_{9,11}$
A_1	3067	3071	3071	3071	3069	3069	3069
	3054	3061	3061	3061	3060	3060	3060
	3067	3057	3057	3057	3049	3049	3049
	1004	992	992	992	978	978	978
	1211	1255	1230	1250	1250	1255	1255
	521	487	485	480	483	483	483
	786	780	780	775	776	776	776
	2920	2900	2900	2897	2900	2900	2900
	2981	2976	2976	2966	2976	2976	2976
	1504	1496	1490	1496	1493	1493	1493
	1181	1181	1181	1181	1181	1181	1181
	1605	1631	1622	1630	1630	1630	1630
	895	911	911	911	903	903	903
	1462	1464	1463	1462	1464	1464	1464
	1380	1380	1380	1369	1380	1380	1380
	1040	1045	1038	1039	1045	1045	1045
	729	747	747	747	747	747	747
	702	693	692	693	690	690	690
	1031	1022	1022	1022	1021	1021	1021
	217	204	203	203	203	203	203
	463	443	436	443	441	441	441
	993	962	961	959	962	962	962
A_2	3074	3064	3064	3064	3064	3064	3064
	3032	3056	3056	3056	3056	3056	3056
	623	612	612	612	611	611	611
	1278	1304	1300	1304	1293	1295	1295
	346	290	288	287	290	290	290
	2981	2977	2976	2966	2977	2977	2977
	1439	1431	1426	1430	1424	1424	1424
	1136	1173	1172	1172	1172	1172	1172
	1331	1327	1317	1326	1327	1327	1327
	1090	1076	1074	1075	1073	1073	1073
	1586	1614	1597	1634	1598	1598	1598
	1462	1466	1465	1465	1462	1462	1462
	970	967	967	964	967	967	967
	970	970	970	967	970	970	970
	842	845	845	845	845	845	845
	414	398	398	398	398	398	398

β-factors. The cyclohexane molecule, owing to the equivalents of all the carbon atoms, is characterized by a single thermodynamic isotopic factor, whose values for different temperatures are in Table 15.

TABLE 13. THERMODYNAMIC ISOTOPIC FACTORS OF AROMATIC HYDROCARBONS /51

T, K	Benzene	Toluene			
	β_{Σ}- factor	β_{Σ}- factor	β_i - factors		
			β_{C_4}	$\beta_{C_{10}}$	$\beta_{C_7}=\beta_{C_{8,12}}=\beta_{C_{9,11}}$
100	1,7792	1.7747	1,6182	1,8728	1,7864
200	1,2815	1.2801	1.2318	1,3099	1,2839
300	1,1533	1,1527	1,1293	1,1677	1,1545
400	1,0975	1.0972	1,0840	1,1057	1,0982
500	1,0676	1.0674	1,0593	1,0725	1,0680
600	1,096	1.0494	1.0443	1,0527	1.0498
700	1,0380	1,0378	1.0343	1,0399	1,0381
800	1,0300	1.0289	1,0273	1.0312	1,0300
900	1,0242	1,0240	1,0223	1,0250	1,0242
1000	1.0200	1.0198	1.0185	1,0205	1,0200
1100	1.0167	1,0166	1,0156	1,0171	1,0167
1200	1,0142	1.0141	1.0134	1,0144	1.0142
1300	1,0122	1,0121	1.0115	1.0124	1,0122
1400	1,0106	1,0105	1.0101	1,0107	1,0106
1500	1,0093	1,0092	1,0088	1,0094	1,0093

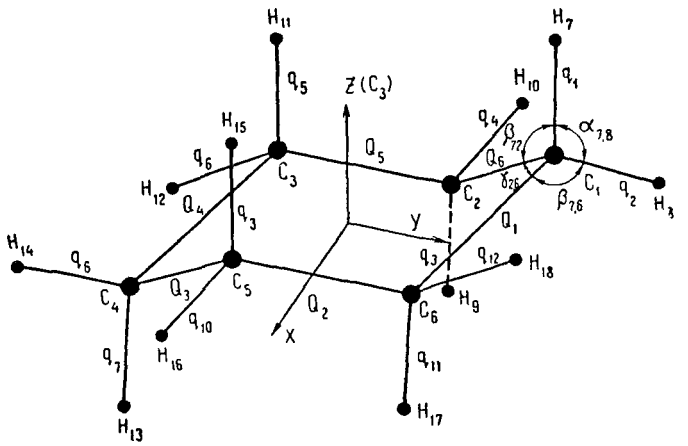


Fig. 8. Cyclohexane molecule

Heteroatomic Organic Compounds

Acetic Acid

CH_3COOH

Geometry. The configuration of the acetic acid molecule is given in Fig. 9. The parameters are: r_{C-H} = 1.093 AU, r_{C-C} = 1.49 AU, $r_{C=O}$ = = 1.213 AU, $r_{C=O}$ = 1.373 AU, r_{O-H} = 1.097 AU, $\alpha = \beta =$ = 109°28', $\delta_1 = \delta_2 = \gamma =$ = ϕ = 120°.

Force constants. By combining the force fields of the alkyl radicals and the carboxyl group, the force constants are obtained. The complete system of force constants used in calculating the isotopic frequencies are in /42/.

TABLE 14. VIBRATIONAL FREQUENCIES OF ISOTOPIC SPECIES OF CYCLOHEXANE /53

Vibration class	Frequency number	Observed ν, cm^{-1}	Calculated ν, cm^{-1}	
			$C_6^{12}H_{12}$	$C_6^{13}H_{12}$
A_{1g}	1	2941	2973	2969
	2	2852	2871	2868
	3	1445	1433	1432
	4	1158	1174	1173
	5	802	783	770
	6	384	315	313
A_{2g}	7	1355	1380	1369
	8	1117	1126	1113
A_{1u}	9	1377	1393	1387
	10	1150	1167	1152
	11	1127	1141	1140
A_{2u}	12	2932	2945	2940
	13	2862	2926	2921
	14	1456	1456	1454
	15	905	957	945
	16	521	476	473
E_g	17	2924	2929	2922
	18	2886	2873	2870
	19	1445	1443	1440
	20	1348	1370	1369
	21	1267	1274	1268
	22	1029	1077	1069
	23	785	762	756
	24	427	415	409
E_u	25	2932	2947	2947
	26	2862	2904	2901
	27	1456	1449	1447
	28	1342	1366	1357
	29	1262	1274	1268
	30	905	914	904
	31	862	863	856
	32	248	178	177

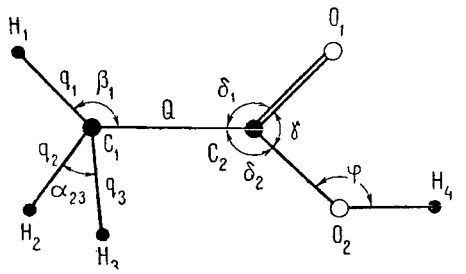


Fig. 9. Acetic acid molecule

Symmetry and vibration classes. Point group is C_s. Irreducible representation: $\Gamma = 12A' + 6A''$. Besides the coordinates describing the change in valency bonds and angles (see Fig. 9), the coordinates describing

TABLE 15. THERMODYNAMIC ISOTOPIC FACTORS (β_{Σ}-FACTORS) OF CYCLOHEXANE AND OTHER HYDROCARBONS /54

T, K	Naphthenic	Aromatic		Paraffinic			
	cyclohexane	benzene	toluene	ethane	propane	butane	pentane
100	1.7800	1.7792	1.7747	1.5967	1.6533	1.6810	1.697
200	1.2828	1.2815	1.2801	1.2333	1.2478	1.2553	1.259
300	1.1544	1.1533	1.1527	1.1317	1.1385	1.1419	1.145
400	1.0983	1.0975	1.0972	1.0861	1.0896	1.0915	1.092
500	1.0683	1.0679	1.0674	1.0610	1.0630	1.0641	1.064
600	1.0502	1.0496	1.0494	1.0455	1.0468	1.0475	1.047
700	1.0384	1.0380	1.0378	1.0353	1.0351	1.0366	1.036
800	1.0364	1.0300	1.0298	1.0282	1.0288	1.0297	1.029
900	1.0246	1.0242	1.0240	1.0229	1.0233	1.0236	1.023
1000	1.0203	1.0194	1.0198	1.0191	1.0193	1.0195	1.019
1100	1.0170	1.0167	1.0166	1.0161	1.0163	1.0164	1.016
1200	1.0145	1.0142	1.0141	1.0138	1.0139	1.0140	1.014
1300	1.0124	1.0122	1.0121	1.0119	1.0120	1.0121	1.012
1400	1.0108	1.0106	1.0105	1.0104	1.0105	1.0106	1.010
1500	1.0095	1.0093	1.0092	1.0091	1.0091	1.0092	1.009

internal rotations (τ_1, τ_2) and the projections of bonds from the plane (ρ_1, ρ_2, ρ_3) were calculated. The complete spectrum of isotopic frequencies is given in Table 16.

β-factors. Acetic acid has two β-factors: one characterizing the carbon atom of the CH_3 group, and the other -- the carbon atom of the carboxyl group (Table 17).

Methyl Alcohol CH_3OH

Geometry. The configuration of the methyl alcohol molecule is shown in Fig. 10. The parameters are: $r_{C-H} = 1.093$ AU, $r_{C-O} = 1.427$ AU, $r_{O-H} = 0.956$ AU, $\alpha = \beta = 109^{\circ}28'$, $\delta_1 = 108^{\circ}52'$.

Force constants. The force field adopted is given in /42/.

Symmetry and vibration classes. Point group is C_s. Irreducible representation: $\Gamma = 8A' + 4A''$. The calculated frequencies are given in Table 16.

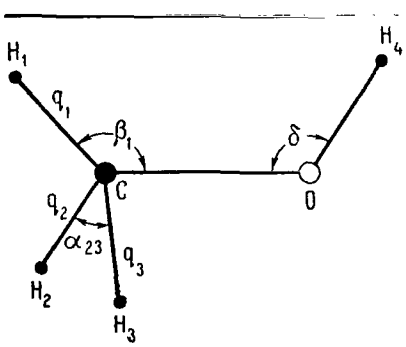
β-factor. It has a single value (see Table 17).

TABLE 16. FREQUENCY OF ISOTOPIC FORMS OF HETEROATOMIC ORGANIC COMPOUNDS (IN cm-1)

/55

Vibration class	Frequency number	Acetic acid				Acetaldehyde				Methylamine			Methyl alcohol		
		Obs.	Calculated			Obs.	Calculated			Obs.	Calc.		Obs.	Calc.	
		Basic form		CH_3-	-COOH	Basic form		CH_3-	-CHO	Basic form		CH_3-	Basic form		CH_3-
A'	1	3583	3579	3578	3579	2967	2977	2966	2977	3360	3366	3366	2973	2959	2947
	2	3051	2978	2968	2978	2917	2896	2893	2896	2985	2956	2966	2845	2866	2864
	3	2944	2897	2894	2897	2736	2742	2742	2734	2820	2839	2842	1455	1475	1474
	4	1788	1791	1791	1744	1426	1468	1464	1467	1623	1687	1693	1425	1411	1400
	5	1445	1464	1462	1464	1410	1450	1447	1448	1473	1474	1476	1345	1346	1345
	6	1382	1380	1377	1394	1342	1362	1354	1360	1410	1411	1415	1070	1075	1069
	7	1264	1407	1396	1354	1122	1103	1092	1085	1130	1136	1145	1034	1036	1029
	8	1182	1171	1171	1169	919	961	953	958	1044	1018	1036	—	—	—
	9	989	1066	997	1005	509	539	534	536	780	778	779	—	—	—
	10	847	824	820	823	—	—	—	—	—	—	—	—	—	—
	11	652	654	645	653	—	—	—	—	—	—	—	—	—	—
	12	581	543	540	542	—	—	—	—	—	—	—	—	—	—
A''	1	2996	2976	2965	2976	3024	2974	2964	2973	3423	3430	3430	2973	2958	2946
	2	1445	1471	1469	1471	1441	1467	1466	1467	2985	2957	2968	1475	1474	1473
	3	1048	1108	1099	1096	1104	1051	1008	1014	1485	1503	1508	1160	1091	1083
	4	642	760	759	746	880	898	897	884	1470	1439	1442	270	274	274
	5	534	493	493	492	150	176	176	174	—	831	834	—	—	—
	6	—	112	112	112	—	—	—	—	264	269	269	—	—	—

/57



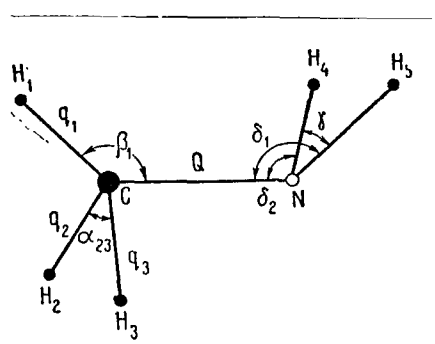


Fig. 10. Methyl alcohol molecule. Fig. 11. Methylamine molecule.

TABLE 17. THERMODYNAMIC ISOTOPIC FACTORS OF HETEROATOMIC ORGANIC COMPOUNDS IN THE 100-1500° K TEMPERATURE RANGE /56

T, K	Acetic acid			Acetaldehyde			Methyl amine	Methyl alcohol
	β_{CH_3}	β_{COOH}	β_Σ	β_{CH_3}	β_{CHO}	β_Σ	$\beta_{CH_3}=\beta_\Sigma$	$\beta_{CH_3}=\beta_\Sigma$
100	1.6608	2.1585	1.9096	1.6951	2.1581	1.8816	1.6157	1.6130
200	1.2485	1.4025	1.3255	1.2329	1.4186	1.3257	1.2398	1.2985
300	1.1385	1.2179	1.1782	1.1313	1.2358	1.1835	1.1361	1.1351
350	1.1100	1.1711	1.1405	1.1047	1.1889	1.1468	1.1087	1.1079
400	1.0898	1.1380	1.1139	1.0867	1.1553	1.1205	1.1089	1.0884
450	1.0747	1.1137	1.0942	1.0715	1.1303	1.1009	1.0745	1.0738
500	1.0633	1.0952	1.0792	1.0607	1.1111	1.0859	1.0632	1.0626
550	1.0541	1.0808	1.0674	1.0521	1.0959	1.0740	1.0543	1.0538
600	1.0471	1.0694	1.0582	1.0453	1.0837	1.0645	1.0472	1.0468
650	1.0413	1.0602	1.0507	1.0388	1.0737	1.0567	1.0414	1.0410
700	1.0365	1.0527	1.0446	1.0352	1.0654	1.0503	1.0366	1.0363
800	1.0291	1.0413	1.0352	1.0281	1.0523	1.0403	1.0292	1.0289
900	1.0237	1.0332	1.0284	1.0229	1.0430	1.0329	1.0238	1.0236
1000	1.0197	1.0272	1.0234	1.0190	1.0359	1.0274	1.0198	1.0196
1100	1.0166	1.0228	1.0197	1.0161	1.0304	1.0232	1.0167	1.0165
1200	1.0141	1.0193	1.0167	1.0137	1.0260	1.0198	1.0143	1.0141
1300	1.0122	1.0165	1.0143	1.0118	1.0225	1.0171	1.0123	1.0122
1400	1.0106	1.0143	1.0124	1.0103	1.0197	1.0150	1.0107	1.0106
1500	1.0094	1.0125	1.0109	1.0097	1.0179	1.0135	1.0094	1.0094

Methylamine CH_3NH_2

Geometry. The configuration of the methylamine molecule is shown in Fig. 11. Parameters: $r_{C-H} = 1.093$ AU, $r_{N-H} = 1.011$ AU, $r_{C-N} = 1.47$ AU, $\alpha = \beta = 1.09°28'$, $\delta_1 = \delta_2 = 112°$, $\gamma = 106°$.

Force constants. The adopted force field is given in /42/.

Symmetry and vibration classes. Point group is C_s. Irreducible representation: $\Gamma = 9A' + 6A''$. The calculated frequencies are in Table 16.

β-factor. It has a single value (see Table 17).

Acetaldehyde CH_3CHO

Geometry. The configuration of the acetaldehyde molecule is shown in Fig. 12. The parameters are: $r_{C-H(CH_3)} = 1.093$ AU, $r_{C-C} = 1.501$ AU, $r_{C=O} = 1.216$ AU, $r_{C-H(CHO)} = 1.114$ AU, $\alpha = \beta = 109°28'$, $\delta_1 = \delta_2 = 126°$, $\gamma = 108°$.

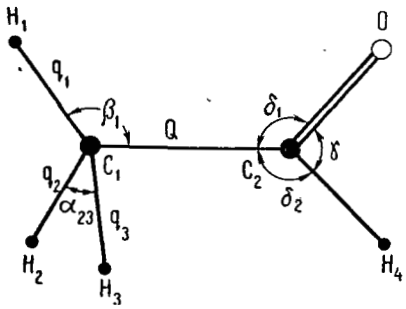


Fig. 12. Acetaldehyde molecule

Force constants. They were obtained by combining the force fields of the alkyl radicals and of the aldehyde group. The adopted system of force constants is given in [42].

Symmetry and vibration classes. Point group is C_s. Irreducible representation: $\Gamma = 10A' + 5A''$. The calculated vibrational spectrum of isotopic species is shown in Table 16.

TABLE 18. RATIOS OF DISTRIBUTION FUNCTIONS OF ISOTOPIC SPECIES OF ACETALDEHYDE [174] /58

T, K	$\frac{CH_3C^{13}HO}{CH_3C^{12}HO}$	$\frac{C^{13}H_3CHO}{C^{12}H_3CHO}$	T, K	$\frac{CH_3C^{13}HO}{CH_3C^{12}HO}$	$\frac{C^{13}H_3CHO}{C^{12}H_3CHO}$
273.15	1.184	1.161	400	1.102	1.043
300	1.160	1.141	450	1.085	1.077
350	1.126	1.113	500	1.071	1.066

β-factors. Acetaldehyde has two β_i-factors: one characterizes the carbon atom of the CH_3 group, and the other -- the carbon atom of the aldehyde group (see Table 17).

The acetic acid molecule was also calculated by H. Johansen [174], who obtained the ratios of the distribution functions given in Table 18.

In addition to acetaldehyde, H. Johansen calculated a series of molecules that have no geochemical significance, but information about the isotopic properties of these molecules is vital for the analysis of general correlations of isotope effects of organic compounds. Below are given the corresponding data.

Propynal C_2HCHO

The configuration of the propynal molecule is in Fig. 13. The parameters are: r = 1.08 AU. s = 1.21 AU, R = 1.46 AU, v = = 1.06 AU, S = 1.204 AU, $\delta = \gamma = 120^\circ$, $\phi_1 = \psi = 180^\circ$.

There are three nonequivalent carbon atoms in the propynal molecule. Therefore, the compound is characterized by three β_i-factors corresponding to the isotopic species $C_2HC^{13}HO(\beta_I)$, $C_I^{13}CHCHO(\beta_{II})$ and $C_IC^{13}HCHO(\beta_{III})$; the remaining values are not independent (Table 19). H. Johansen gives a redundant system of values. As can easily be seen, $f_1 = \beta_I$, $f_2 = \beta_{II} = \beta_{III}$, $f_3 = \beta_I\beta_{II}\beta_{III}$, $f_4 = \beta_{II}$, $f_5 = \beta_{III}$, $f_6 = \beta_{II}\beta_{III}$, $f_7 = \beta_I$ and $f_8 = \beta_I\beta_{III}$, therefore in the following for the molecules calculated by H. Johansen we will give only the independent values of the β_i-factors in our understanding.

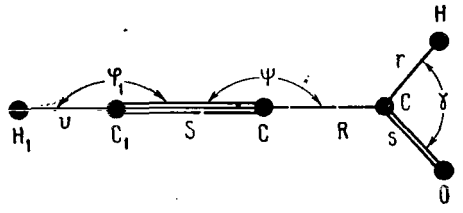


Fig. 13. Propynal molecule

Monochloroacetic Acid $CClH_2COOH$

The configuration of the molecule is shown in Fig. 14. The parameters are: $\ell_1 = \ell_2 = 1.12$ AU, $\ell_3 = 1.78$ AU, R = 1.49 AU, s = 1.213 AU, t = 1.368 AU, u = 1.097 AU, $\alpha_i = \beta_i = 109^\circ28'$, $\delta = \eta = \sigma = 120^\circ$.

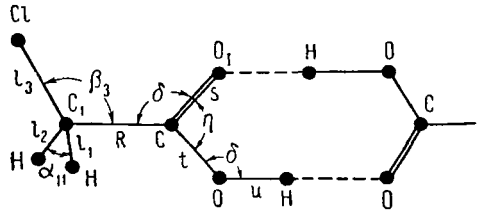


Fig. 14. Monochloroacetic acid molecule

Monochloroacetic acid is trimorphous. One of the three forms (α-form) is stable. A dimer is also possible. The monomeric α-form was calculated (Table 20).

Formic Acid HCOOH

The configuration of the molecule is in Fig. 15. The parameters are: r = 1.09 AU, s = = 1.213 AU, t = 1.368 AU, $\sigma = 107^\circ$, $\gamma = \eta = 120^\circ$. The results of the calculations are in Table 21.

TABLE 19. RATIO OF DISTRIBUTION FUNCTIONS OF ISOTOPIC SPECIES OF PROPYNAL [174] /59

T, K	f_1 $\frac{C_2HC^{13}HO}{C_2HC^{12}HO}$	f_2 $\frac{C_2^{13}HCHO}{C_2^{12}HCHO}$	f_3 $\frac{C_2^{13}HC^{13}HO}{C_2^{12}HC^{12}HO}$	f_4 $\frac{C_1^{13}CHCHO}{C_1^{12}CHCHO}$
273.15	1.196	1.282	1.537	1.133
300	1.170	1.246	1.461	1.117
350	1.134	1.196	1.359	1.094
400	1.109	1.160	1.288	1.078
450	1.090	1.134	1.238	1.066
500	1.076	1.114	1.199	1.056

T, K	f_5 $\frac{C_2^{13}HCHO}{C_1^{12}CHCHO}$	f_6 $\frac{C_2^{13}HC^{13}HO}{C_2HC^{12}HO}$	f_7 $\frac{C_2^{13}HC^{13}HO}{C_2^{13}HCHO}$	f_8 $\frac{C_2^{13}HC^{13}HO}{C_1^{13}CHCHO}$
273.15	1.132	1.285	1.199	1.357
300	1.116	1.248	1.173	1.308
350	1.093	1.198	1.136	1.242
400	1.077	1.162	1.110	1.195
450	1.064	1.135	1.091	1.161
500	1.055	1.115	1.077	1.136

TABLE 20. RATIO OF DISTRIBUTION FUNCTIONS OF ISOTOPIC SPECIES WITH RESPECT TO CARBON FOR MONOCHLOROACETIC ACID [174] (β_i-FACTORS) /60

T, K	$CClH_2C^{13}OOH$	$C^{13}ClH_2COOH$
273.15	1.204	1.154
300	1.177	1.133
350	1.139	1.04

TABLE 21. RATIO OF DISTRIBUTION FUNCTIONS OF ISOTOPIC SPECIES WITH RESPECT TO CARBON FOR FORMIC ACID [174] (β_i-FACTORS)

T, K	273.15	300	350	400	450	500
$\frac{HC^{13}OOH}{HC^{12}OOH}$	1.228	1.197	1.156	1.126	1.104	1.088

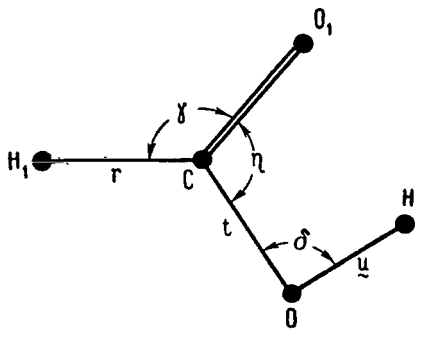


Fig. 15. Formic acid molecule

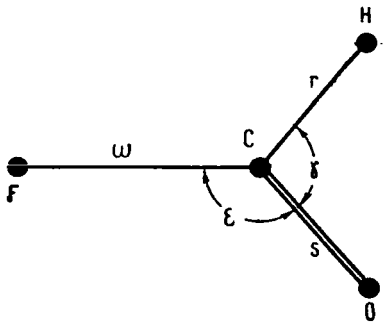


Fig. 16. Formylfluorite molecule

Formylfluorite HCOF /61

The configuration of the molecule is in Fig. 16. The parameters are: r = 1.09 AU, s = 1.192 AU, ω = 1.351 AU, $\epsilon = \gamma = 120^{\circ}$. Results of the calculation are in Table 22.

TABLE 22. RATIO OF DISTRIBUTION FUNCTIONS OF ISOTOPIC SPECIES WITH RESPECT TO CARBON FOR FORMYLFLUORITE /174/ (β_i-FACTORS)

T, K	273.15	300	350
$\frac{HC^{13}OF}{HC^{12}OF}$	1,213	1,186	1,147

Formate Ion $HCOO^-$

TABLE 23. RATIO OF DISTRIBUTION FUNCTIONS OF ISOTOPIC SPECIES WITH RESPECT TO CARBON FOR FORMATE ION /174/ (β_i-FACTORS)

T, K	273.15	300	350	400	450	500
$\frac{HC^{13}OO^-}{HC^{12}OO^-}$	1,186	1,162	1,128	1,103	1,085	1,072

The configuration of the formate ion molecule is given in Fig. 17. The parameters are: r = 1.085 AU, $d_1 = d_2 = 1.27$ AU, $\eta = 125^{\circ}$. Results of the calculation are in Table 23.

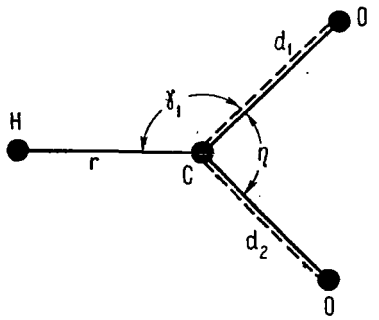


Fig. 17. Formate ion molecule

Inorganic Compounds of Carbon

Simple monoatomic compounds of carbon CO, CO_2, $CO_3^=$, and HCN were calculated by H. Urey /228, 229/. At the present time, there are new spectral data for obtaining revised values of the β-factors. However, the indeterminacies associated with the anharmonicity of the vibrations and the provisionality of the force field overbalance the small gain in precision achieved by using the more exact values of the frequencies. Therefore in Table 24 we give the well-known data of H. Urey unchanged. Added are only the values of the β-factors we calculated for CF_4.

TABLE 24. THERMODYNAMIC ISOTOPIC FACTORS OF INORGANIC COMPOUNDS OF CARBON /62

T, K	CF_4	$CO_3^=$	CO_2	C (diamond)	HCN	CO	CN^-
273.1	1.2603	1.2358	1.2169	1.2081	1.1358	1.1086	1.0980
298.1	1.2241	1.2057	1.1909	1.1786	1.1206	1.0970	1.0875
400	1.1394	1.1274	1.1233	1.1077	1.0802	1.0659	1.0589
500	1.0946	1.0870	1.0877	1.0722	1.0581	1.0479	1.0427
600	1.0682	1.0629	1.0656	1.0516	1.0441	1.0360	1.0323

Y. Bottinga /123/ published calculations for a series of inorganic compounds, mainly already known compounds, but they are of interest in that he examined elemental carbon in the form of graphite (and H. Urey examined it in the form of diamond). In Table 25 the data are given as the partition coefficients, more exactly, as the values of $10^2 \ln \alpha$, which are closely comparable directly with the values C^{13} (percent) of the isotopic shifts $[\Delta C^{13}\% = (\alpha - 1) \times 10^2 = \ln \alpha \cdot 10^2]$

Intermolecular and Intramolecular Thermodynamic Isotope Effects /63

The values calculated for the isotope constants of hydrocarbons and other organic compounds, in combination with the data of H. Urey, H. Johansen, and Y. Bottinga afford quite a detailed picture of the thermodynamic isotopic effects in systems containing carbon compounds.

TABLE 25. VALUES OF $10^2 \ln \alpha$ FOR ISOTOPIC EXCHANGE BETWEEN CARBON DIOXIDE, CALCITE, GRAPHITE, AND METHANE /123/

T, °C	$\frac{CaCO_3}{CH_4}$	$\frac{CO_2}{CH_4}$	$\frac{C(graph.)}{CH_4}$	$\frac{CaCO_3}{C(graph.)}$	$\frac{CO_2}{C(graph.)}$	$\frac{CO_2}{CaCO_3}$
0	9.06	7.77	6.34	2.72	1.43	−1.30
25	7.85	6.83	5.37	2.48	1.46	−1.01
50	6.84	6.07	4.58	2.26	1.49	−0.77
70	6.16	5.55	4.05	2.11	1.50	−0.61
100	5.29	4.89	3.38	1.91	1.51	−0.40
160	4.00	3.89	2.41	1.59	1.48	−0.11
200	3.36	3.39	1.95	1.42	1.44	0.02
300	2.28	2.48	1.18	1.10	1.31	0.21
400	1.63	1.90	0.74	0.88	1.15	0.27
500	1.22	1.49	0.49	0.73	1.01	0.28
600	0.95	1.21	0.33	0.62	0.88	0.26
700	0.77	1.00	0.23	0.54	0.77	0.23

The intermolecular thermodynamic isotopic effect is determined by the ratio of the β-factors (molecular thermodynamic isotopic factors) of the system components. Table 26 gives the values of the β-factors of carbon compounds obtained by quantum-statistical calculation. As will be shown further, applying the method of isotopic bond numbers proposed by the author in principle permits an unlimited expansion of the list given. But these data served as the starting point.

The results of calculating the thermodynamic isotopic effects of polyatomic compounds are vital to our understanding of numerous aspects of the chemistry, geochemistry, and biochemistry of stable isotopes. They can be viewed in many aspects. For purposes associated with the program of studying petroleum hydrocarbons, special significance lies in the phenomenon of intramolecular fractionation of isotopes established here.

As was shown above, polyatomic molecules containing atoms nonequivalent with respect to exchange are characterized by intramolecular isotope effects; in other words, the atoms appearing in various structural groups of a given molecule have different isotopic makeup. Of course, we must bear in mind that the concept "intramolecular" has a statistical significance (that is, it pertains not to a single molecule, but to their set).

The common property of all the compounds investigated is the successive decrease in the thermodynamic isotopic factors with

temperature rise and in addition, the decrease in the ratios of the thermodynamic isotopic factors, that is, the decrease in the thermodynamic isotope effects, with increase in temperature.

Temperature functions of the partition coefficients $\alpha = \beta_{\Sigma_{AX_n}} / \beta_{\Sigma_{BX_m}}$ can be easily traced by analyzing Tables 15 and 17. In the following, in order to avoid the use of cumbersome tables, we will deal with data pertaining only to 300° K. When it is necessary to extend the correlations established to the range of higher temperatures, we must turn to Tables 15 and 17 containing data for the entire temperature range investigated.

Features of the distribution of carbon isotopes in systems containing inorganic carbon compounds were already examined by us /29/, therefore, we will dwell briefly on the characteristics of isotope fractionation in hydrocarbon systems.

The values of the thermodynamic isotopic factors (β_{Σ}-factors) increase with increase in molecular weight (at the same temperature), which corresponds to the successive enrichment in C^{13} in high- /65
molecular members of the system CH_4-C_2H_6-C_3H_8-n-C_4H_{10}-n-C_5H_{12}, in the state of isotope-exchange equilibrium. An intramolecular isotope effect is observed, determined by the relatively reduced values of the β_i-factors of the end groups CH_3, which in the equilibrium state corresponds to the concentration of the light carbon isotope in these groups (Fig. 18).

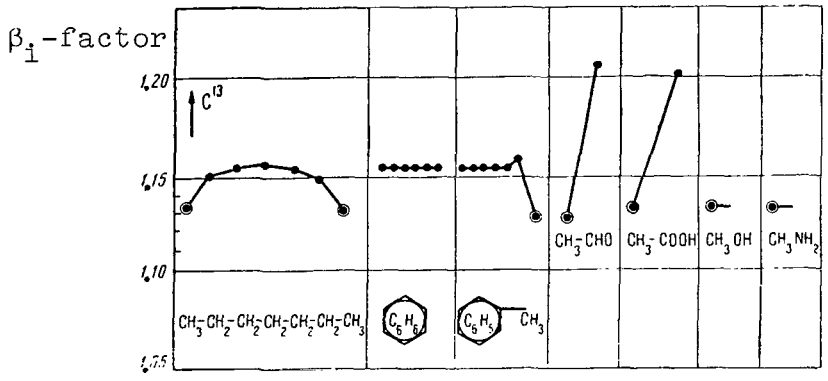


Fig. 18. Intramolecular distribution of carbon isotopes in polyatomic organic compounds

Analysis of the thermodynamic isotopic factors of carbon in aromatic compounds is of interest in the respect that here we encounter a new bond type C-C caused by π-electronic conjugation. The closed π-electron orbit, by Huckel's rule, is characteristic

TABLE 26. THERMODYNAMIC ISOTOPIC FACTORS OF CARBON COMPOUNDS FOR T = 300° K /64

Compound	Molecule	β_Σ	β_i-factors of equivalent atoms		
			β_I	β_{II}	β_{III}
Methane	$\overset{I}{C}H_4$	1.1136	1.1136	—	—
Ethane	$\overset{I}{C}H_3\overset{I}{C}H_3$	1.1317	1.1317	—	—
Propane	$\overset{I}{C}H_3\overset{II}{C}H_2\overset{I}{C}H_3$	1.1385	1.1331	1.1493	—
n-Butane	$\overset{I}{C}H_3\overset{II}{C}H_2\overset{II}{C}H_2\overset{I}{C}H_3$	1.1419	1.1331	1.1507	—
n-Pentane	$\overset{I}{C}H_3\overset{II}{C}H_2\overset{III}{C}H_2\overset{II}{C}H_2\overset{I}{C}H_3$	1.1438	1.1330	1.1506	1.1519
Acetic aldehyde	$\overset{II}{C}H_3\overset{I}{C}HO$	1.151	1.160	1.140	—
Propynal	$\overset{III}{C}H\overset{II}{C}\overset{I}{C}HO$	1.154	1.196	1.132	1.133
Monochloroacetic acid	$\overset{II}{C}ClH_2\overset{I}{C}OOH$	1.155	1.177	1.133	—
Formate ion	$\overset{I}{H}COO^-$	1.162	—	—	—
Formylfluorite	$\overset{I}{H}COF$	1.186	—	—	—
Formic acid	$\overset{I}{H}COOH$	1.197	—	—	—
Acetic acid	$\overset{II}{C}H_3\overset{I}{C}HOH$	1.178	1.218	1.138	—
Methylamine	CH_3NH_2	1.136	—	—	—
Methyl alcohol	CH_3OH	1.135	—	—	—
Benzene	$\overset{I}{C}_6H_6$	1.1533	1.1533	—	—
Toluene	$\overset{I}{C}_5H_5\overset{II}{C}\,\overset{III}{C}H_3$	1.1527	1.1545	1.1677	1.1293
Cyclohexane	$\overset{I}{C}_6H_{12}$	1.1544	1.1544	—	—
Carbon tetrachloride	CF_4	1.2241	—	—	—
Carbon dioxide	CO_2	1.1909	—	—	—
Carbon monoxide	CO	1.0970	—	—	—
Carbonate ion	$CO_3^=$	1.2057	—	—	—
Hydrogen cyanide	HCN	1.1206	—	—	—
Cyanide	CN^-	1.0875	—	—	—
Graphite, diamond	C	1.1786	—	—	—

of cyclic structures containing $4n + 2$ π-electrons (where $n = 0, 1, 2, \ldots$). A typical representative of this kind of compound is benzene, in which six π-electrons form a closed ring-like π-electronic cloud. Toluene was selected in order to investigate the effect of the alkyl substituent both on the thermodynamic isotopic factor of the alkylated aromatic compound, as well as on the distribution of the values of the β-factors characterizing the carbon atoms in the aromatic ring.

We can draw the following conclusions from these data.

Thermodynamic isotopic factors of aromatic compounds have larger values than the thermodynamic isotopic factors of aliphatic

hydrocarbons at the same temperatures. Therefore, at isotope exchange equilibrium, the former must be enriched in the heavy carbon isotope compared with the latter. /66

The thermodynamic isotopic factor of benzene (β_Σ) and of its alkyl-substituted derivative -- toluene -- are close. In other words, in contrast to the system of normal alkanes, the separation of isotopes between aromatic homologs is slight.

Toluene is characterized by intramolecular thermodynamic effects caused by the difference in the β_i-factors characterizing replacement at the carbon of the metal radical, on the one hand, and at the carbon atoms of the rings -- on the other. In addition, in the ring itself the β_i-factor characterizing the atom in the ring, bound directly to the radical has an increased value. This means, first, that in the equilibrium toluene molecule the carbon in the side group is enriched in the light isotope relative and, second, that the total carbon in the aromatic ring is characterized by a higher content of the heavier isotope than the carbon of benzene in equilibrium with it, that is, in the formation of the alkylated carbon there is an increase in the ability of the aromatic ring to concentrate the heavy isotope.

As follows from Table 15, the thermodynamic isotopic factor of cyclohexane is larger than for normal alkanes, and is close to the thermodynamic isotopic factors of aromatic compounds. Therefore, in the equilibrium isotope-exchange system, alicyclic and aromatic hydrocarbons can have the same isotopic composition and differ here by a higher concentration of C^{13} compared to paraffinic compounds. Since cyclohexane, on the one hand, is close to the alkanes (in bond nature), and on the other -- to benzene (by virtue of the cyclic structure), this means that cyclicity is a determining feature from the standpoint of isotopic properties. The appearance, however, of the strong π-conjugation in the aromatic ring compared with the ordinary type of σ-bonds characterizing cyclohexane does not introduce appreciable changes into the nature of the isotope effects.

A feature of heteroatomic organic compounds is the increased value of the β_i-factors characterizing the carbon of the functional group. In particular, as follows from our calculations, β_i-factors of carbon in the carboxyl and aldehyde groups are considerably higher than the β_i-factors of the carbon in the alkyl radical, which in the case of equilibrium distribution of isotopes corresponds to the accumulation in these groups of the heavy carbon isotope. The same derives from the data of H. Johansen for propynal, formic acid, and monochloroacetic acid.

The variations of the β-factors for alkyl radicals as a function of the addition of various functional groups are slight. The value of the β-factor of the CH_3 group of the aldehyde drops somewhat. Evidently, this can be accounted for by the less successful choice of the force field, which is confirmed by the poorer comparability of observed and calculated frequencies in this case. /67

The necessity of taking account of intramolecular isotope effects requires that in the tables characterizing the separation of isotopes there be included not only the values of the reduced thermodynamic isotopic factors β_Σ, but also the values of the β_i-factors or the thermodynamic isotopic factors of the main isotopic species β_q (see Table 26).

Introducing the concept of the thermodynamic isotopic factor permits tabulating these quantities instead of the earlier-used tabulation of the partition coefficients α. In setting up the tables of the values of α, certain inconveniences arise (they have to be imaged in the pattern of a football or chessboard layout) /29, 68, and so on/, and in addition, here the values pertain not to compounds, but to systems, which contradicts the traditional rule of chemistry according to which values pertaining not to reactions (systems), but to compounds must be tabulated.

CHAPTER TWO /68

BIOGENIC ISOTOPIC EQUILIBRIA.

Isotopic Bond Numbers

Calculation of thermodynamic isotopic factors is quite a laborious problem, especially when we are dealing with complicated organic molecules. Moreover, in several cases in general it is impossible to get reliable values of β-factors, for example, if there are no data on the vibrational spectrum of the compound investigated, or if these data are incomplete. Therefore it is extremely tempting to search for correlations determining the thermodynamic isotopic factor, on the basis of which one could more or less reliably predict the β-factors of as yet uninvestigated (by calculation) compounds.

Upon analysis of Table 26 in which are presented the known values of the β_{Σ}-factors and the β_i-factors of individual structural components of these compounds calculated for 300° K, it is difficult to detect at first glance any internal unity of these quantities.

It can be assumed that the higher the number of hydrogen atoms that a carbon atom is associated with, the smaller is the β-factor characterizing it. For example, carbon in methane forming the 4(C-H)-bonds has a β-factor of 1.113. The carbon in the CH_3 group appearing, for example, in methane, forms 3(C-H) bonds and a C-C bond and has a higher β_i-factor -- 1.132. Even higher is /69 the value of the β_i-factor of the CH_2 group, the carbon of which, appearing in propane (1.149) or pentane (1.151 and 1.152), forms 2(C-H) bonds and 2(C-C) bonds, while carbon tetrachloride, not having a single (C-H) bond, has a very high β-factor -- 1.217. This is so on the one hand. And on the other, the carbon in propynal forming a single bond with hydrogen, has a β-factor

(1.133) that is close to the β-factors of the structural components in which the carbon has 3(C-H) bonds. The carbon appearing in the naphthenic ring and forming 2(C-H) bonds is characterized by the same β-factor (1.154) as the carbon appearing in the benzene ring and forming 1(C-H) bond (1.153). Finally, the carbon monoxide, in which there are no C-H bonds, has the lowest β-factor (1.097) of the carbon compounds investigated. Thus, the β_i-factor is not directly determined by the number of (C-H) bonds or by their actions.

Even less definite is the correlation between the values of the β-factors and the structural position of the carbon. For the homologous series of methane there exists, as was shown above, a quite well-defined additive dependence of the β_Σ-factors of normal alkanes, making it possible through extrapolation to establish the β_Σ-factor for the higher members of this series. However, methane itself is an exception. The β_Σ-factors of the cyclic hydrocarbons as a whole are higher than for the aliphatic hydrocarbons. Carbon of the functional groups, as a rule, is marked by higher values of the β-factors, but the range of fluctuations in the β-factors within the limits of each of the structural groups is very appreciable.

Heteroatomic organic compounds and inorganic compounds of carbon to the first approximation seemingly have higher β-factors than do the hydrocarbons. Actually, compounds such as CF_4, CO_2, and $CO_3^=$ are characterized by the largest β-factors (1.217, 1.191, and 1.206, respectively). From this standpoint, it is easy to account for the increased β-factors appearing in the functional groups of organic compounds. However, the carbon of these heteroatomic compounds, such as methyl alcohol and methylamine, are marked by very low β-factors (1.135 and 1.136, respectively). An even lower value (minimum) is found for such a simple inorganic compound as CO.

Thus, none of these approaches enables us to establish stable correlations that could be extended to all carbon compounds. But here we must remember that when calculating the vibrational frequencies of molecules, the principle of the transferral of force constants characterizing the interactions of atoms in some molecules to other molecules containing similar structural components or bonds proves highly fruitful. Vibrational frequencies of compounds calculated from a strong field represented by a set of force /70
constants determined for the corresponding interactions in other compounds as a rule prove to be in satisfactory agreement with the experimentally observed frequencies.

Accordingly, a question arises as to whether the actual value of the β-factor can be represented as some combination of numerical values, each of which characterizes a bond type and which appears with identical values in the β-factors of the compounds that include the given bond type. This numerical value would be none other than the end result of the entire total of mathematical transformations performed on some set of dynamic and kinematic elements of the secular equation matrices, which for the same bond type are included virtually in unchanged form in the initial information, but for each compound again run through the entire cycle of the solution all the way up to the obtaining of the β-factor. In other words, this numerical value would be a kind of numerical operator replacing the set of mathematical operations performed on the set of elements of the F- and G-matrices characterizing the given bond type. Further, if thus we succeed in establishing the numerical values for all possible bond types found in organic compounds, this would signify the possibility of finding the β-factors of any organic compounds without first solving the vibrational problem, through a simple combination of a set of numbers characterizing bond types appearing in the compounds of interest to us, which overall would determine the value of the β-factor we seek. Guided by these considerations, we attempted to find these numerical values and arrived at a method, whose essentials are briefly outlined below.

It turned out that the β_i-factor characterizing the carbon atom in any structural position in any compound can be expressed with this relation:

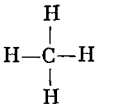
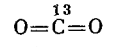
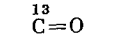
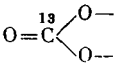
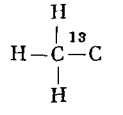
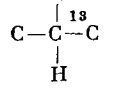
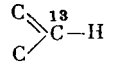
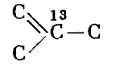
$$\beta = \left(1 + \sum_j^m L_j\right) + \Delta, \qquad \text{(II.1)}$$

where L_j is the sum number characterizing the given bond type. Here the bond numbers have the following values: $L_{C-H} = 0.0285$; $L_{C-C} = 0.046$; $L_{C=C} = 0.062$; $L_{C-C} = 0.078$; $L_{C-N} = 0.052$; $L_{C-O} = 0.055$; $L_{C=O} = 0.095$; $L_{C\equiv C} = 0.066$; $L_{C-F} = 0.056$; $L_{C\equiv N} = 0.091$.

Table 27 presents a comparison of the β_i-factors calculated with the aid of isotopic bond numbers based on Eq. (II.1) and those found directly by solving the vibrational problem for the corresponding isotopic species of the compounds on an electronic computer.

As is clear from Table 27, for nearly all the compounds investigated there is very satisfactory agreement among the β-factors found via the isotopic bond numbers and those calculated from data on the vibrational spectra of the isotopic species. /74

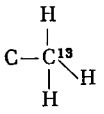
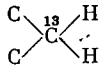
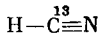
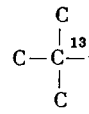
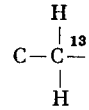
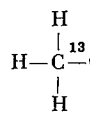
TABLE 27. COMPARISON OF VALUES OF β_i-FACTORS CALCULATED ON AN ELECTRONIC COMPUTER AND THOSE FOUND BY THE ISOTOPIC BOND NUMBER METHOD /71

Compound (structural group)	Structural position of carbon atom	Bonds	β_i-factor: Calc. on comp.	β_i-factor: Calc. via bond nrs.	Corrections Δ
1	2	3	4	5	6
Methane		$4L_{C-H}$	1.114	1.114	0.000
Carbon dioxide		$2L_{C=O}$	1.191	1.192	−0.001
Carbon monoxide		$L_{C=O}$	1.097	1.096	+0.001
Carbonate ion		$2L_{C-O}L_{C=O}$	1.205	1.206	−0.001
Ethane		$3L_{C=H}L_{C-C}$	1.132	1.132	0.000
Propane		$2L_{C-H}2L_{C-C}$	1.149	1.149	0.000
Benzene		$L_{C-H}2L_{C\geq C}$	1.153	1.153	0.0000
Toluene (ring atom bound to methyl group)		$L_{C-C}2L_{C\geq C}$	1.168	1.170	−0.002

Essentially, the same system of isotopic bond numbers describes β-factors of both organic and inorganic compounds of carbon, of both simple molecules as well as complex polyatomic compounds. The Δ values would be viewed as structure corrections, however, they are small for most compounds, therefore we can state that the β-factor first of all is determined by the nature of the chemical bonds forming the compound and, probably, to a slight extent -- by its structure.

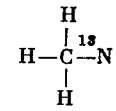
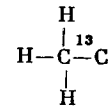
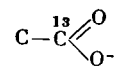
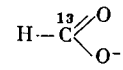
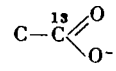
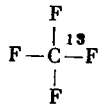
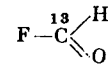
TABLE 27 /continued/

/72

Compound (structural group)	Structural position of carbon atom	Bonds	β_i-factor: Calc. on comp.	β_i-factor: Cal. via bond nrs	Corrections Δ
1	2	3	4	5	6
Toluene (methyl group carbon)		$3L_{C-H}L_{C-C}$	1.129	1.131	−0.002
Cyclohexane		$2L_{C-H}2L_{C-C}$	1.154	1.149	+0.005
Hydrogen cyanide		$L_{C-H}L_{C\equiv N}$	1.120	1.120	0.000
Elemental carbon (graphite, diamond)		$4L_{C-C}$	1.179	1.184	−0.005
Cyanide		$L_{C\equiv N}$	1.088	1.091	−0.003
Acetic aldehyde (functional group)		$L_{C-H}L_{C-C}L_{C=O}$	1.236 1.160*	1.170	+0.066 −0.010
Acetic aldehyde (radical)		$3L_{C-H}L_{C-C}$	1.131 1.141*	1.132	−0.001 +0.010
Propynal (functional group)		$L_{C-H}L_{C-C}L_{C=O}$	1.170	1.171	−0.001
Propynal (radical)		$L_{C-H}L_{C\equiv C}$	1.116	1.116	0.000
Methyl alcohol		$3L_{C-H}L_{C-O}$	1.135	1.140	−0.005

The correspondence is somewhat worse for compounds containing functional groups. Possibly, in this case the individual features of the compounds play a major role. But the discrepancy can be accounted for also by the inadequate reliability of the spectrally calculated β-factors. In any case, the reliability of the isotopic frequencies and β-factors we obtained for heteroatomic organic compounds is considerably less than for hydrocarbons. Judging from the data in Table 16, the discrepancy between the calculated and observed frequencies is greater than usual. This discrepancy

TABLE 27 /conclusion/ /73

Compound (structural group)	Structural position of carbon atom	Bonds	β-factor: Calc. on comp.	β-factor: Cal. via bond nrs	Corrections Δ
1	2	3	4	5	6
Methylamine		$3L_{C-H}L_{C-N}$	1.136	1.137	−0.001
Acetic acid (radical)		$3L_{C-H}L_{C-C}$	1.138	1.132	+0.006
Acetic acid (functional group)		$L_{C-C}L_{C-O}L_{C=O}$	1.218	1.197	+0.021
Formic acid (functional group)		$L_{C-H}L_{C-O}L_{C=O}$	1.197*	1.180	+0.017
Monochloroacetic acid (functional group)		$L_{C-C}L_{C-O}L_{C=O}$	1.177*	1.197	−0.020
Carbon tetrachloride		$4L_{C-F}$	1.217	1.224	−0.007
Formylfluorite		$L_{C-H}L_{C=O}L_{C-F}$	1.186	1.181	+0.005

* Values obtained for analogous structural groups by H. Johansen /174/.

is especially noticeable for acetic aldehyde. For the aldehyde group, we and H. Johansen obtained widely differing β-factors: 1.236 and 1.160 /174/. The β-factor determined by summation of bond numbers is 1.170. Similar discrepancies, as can be seen in Table 27, also occur for the carboxyl group. It is not precluded that the β-factors obtained for this case through summation of the isotopic bond numbers can prove closer to the true values than those calculated based on the not too reliable system of force constants. /74

Thus, by means of the formalism developed here it is possible to a good approximation to arrive at the β-factors for various compounds. This bears above all obvious practical significance, since the extremely laborious and expensive operation (considering the large outlays of highly qualified labor and machine time) which is represented by the solution of the vibrational problem and the determination of the β-factor for a complex compound can be reduced to the elementary addition of several numerical operators. But this is also important for our understanding of the essential nature of the thermodynamic isotope effects and possibly of the nature of the chemical bonds, since in the correlations of the formation of the thermodynamic isotope factor there opens up a pattern of the astonishing unity of compounds that are apparently widely removed in chemical form.

We can attempt to estimate the general form of the formula for the β-factor expressed in terms of this kind of numerical operator.

Let us start from the general expression for the β-factor: /75

$$\beta = \prod_i^n \frac{u_i^* \operatorname{sh} \frac{u_i}{2}}{u_i \operatorname{sh} \frac{u_i^*}{2}}. \qquad \text{(II.2)}$$

Introducing the notation $a = \frac{hc}{2kT}$, which is the hyperbolic sine in terms of the difference between the degrees of the natural logarithm base and converting to frequencies $\tilde{\nu}$, we will have:

$$\beta = \prod_i^n \frac{\tilde{\nu}_i^* \left(e^{a\tilde{\nu}_i} - e^{-a\tilde{\nu}_i}\right)}{\tilde{\nu}_i \left(e^{a\tilde{\nu}_i^*} - e^{-a\tilde{\nu}_i^*}\right)}. \qquad \text{(II.3)}$$

When T = const, a is a constant, and for T = 300° K, a = $= 2.4 \cdot 10^{-3}$. Since in most cases vibrational frequencies are of the order of 10^3 cm^{-1}, we can neglect the value of $e^{-a\tilde{\nu}_i}$ compared with $e^{a\tilde{\nu}_i}$. Frequencies of the isotopically replaced species are smaller than for the basic species: $\nu_i > \tilde{\nu}_i^*$ or $\tilde{\nu}_i^* = \tilde{\nu}_i - \Delta\tilde{\nu}_i$.

With reference to the foregoing, let us reduce Eq. (II.3) to the form

$$\beta = \prod_i^n \frac{\tilde{\nu}_i^*}{\tilde{\nu}_i} e^{a\Delta\tilde{\nu}_i}. \qquad \text{(II.4)}$$

Let us represent the exponent in the right-hand side as the series

$$e^{a\Delta\tilde{\nu}_i} = 1 + \frac{a\,\Delta\tilde{\nu}_i}{1!} + \frac{(a\,\Delta\tilde{\nu}_i)^2}{2!} + \ldots$$

and, considering that $a\Delta\tilde{\nu}_i \ll 1$, let us limit ourselves for simplicity to the first two members of the series:

$$\beta = \prod_i^n \frac{\tilde{\nu}_i^*}{\tilde{\nu}_i}\,(1 + a\Delta\tilde{\nu}_i) = \prod_i^n \frac{\tilde{\nu}_i^*}{\tilde{\nu}_i} \prod_i^n (1 + a\Delta\tilde{\nu}_i) \approx$$

$$\approx \prod_i^n \frac{\tilde{\nu}_i^*}{\tilde{\nu}_i} \left(1 + a \sum_i^n \Delta\tilde{\nu}_i\right). \qquad \text{(II.5)}$$

It should be noted that owing to the simplifications made, this expression cannot be used for an exact calculation of the thermodynamic isotopic factor in terms of isotopic frequencies, but it quite closely reflects the general nature of the dependence of the β-factor on the absolute frequencies and on their isotopic shifts.

Now let us look at the equation of the vibrational motion of a molecule. In matrical form, the secular equation is described as follows: /76

$$\begin{vmatrix} \{GF\}_{11} - \lambda & \{GF\}_{12} & \{GF\}_{13} & \ldots & \{GF\}_{1n} \\ \{GF\}_{21} & \{GF\}_{22} - \lambda & \{GF\}_{23} & \ldots & \{GF\}_{2n} \\ \{GF\}_{31} & \{GF\}_{32} & \{GF\}_{33} - \lambda & \ldots & \{GF\}_{3n} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \{GF\}_{n1} & \{GF\}_{n2} & \{GF\}_{n3} & \ldots & \{GF\}_{nn} - \lambda \end{vmatrix} = 0. \qquad \text{(II.6)}$$

It can be expanded into a polynomial:

$$\lambda^n - c_1\lambda^{n-1} - c_2\lambda^{n-2} - \ldots - c_{n-1}\lambda - c_n = 0. \qquad \text{(II.7)}$$

As we know, the sum of the roots λ is equal to the trace of the secular equation matrix

$$\sum_i^n \lambda_i = \text{Spur}\,\mathbf{GF}. \qquad \text{(II.8)}$$

Therefore,

$$\sum_{i}^{n} \lambda_i = \sum \{GF\}_{ii}. \qquad \text{(II.9)}$$

An element of the GF-matrix can be represented in terms of elements of the G- and F-matrix as follows:

$$\{GF\}_{il} = \sum_{k}^{n} \{G\}_{ik} \{F\}_{kl} \qquad \text{(II.10)}$$

and

$$\sum_{i}^{n} \{GF\}_{ii} = \sum_{i}^{n} \sum_{k}^{n} \{G\}_{ik} \{F\}_{ki}. \qquad \text{(II.11)}$$

Similarly, for an isotopically-replaced molecule

$$\sum_{i}^{n} \lambda_i^* = \sum_{i}^{n} \sum_{k}^{n} \{G^*\}_{ik} \{F^*\}_{kl}. \qquad \text{(II.12)}$$

Noting that the F-matrices, that is, the force constant for isotopic molecules, are equal, we get:

$$\sum_{i}^{n} \Delta\lambda = \sum_{ik}^{n} [\{G\}_{ik} - \{G^*\}_{ik}] \{F\}_{ki}. \qquad \text{(II.13)}$$

Corresponding to a bond molecule is a set of coordinates whose interaction is described by the corresponding elements of the G- and F-matrices. The right-hand side of Eq. (II.13) is the sum of the products of force constants by the difference between the corresponding elements of the isotopic G-matrices. Therefore, this sum can be decomposed into a series of subsums, each of which will contain force constants and the elements of kinematic interaction pertaining to the given bond. /77

Generally speaking, an individual bond cannot be described in isolation, since only one single force constant corresponding to the stretching of the given bond is wholly determined by the nature of this bond. The remaining force constants corresponding to the interaction of deformational coordinates and the interaction of stretching coordinates of the given bond with adjoining bonds depend on the angles that the given bond makes with the neighboring bonds (that is, on molecular structure) and on the nature of the latter. However, in absolute magnitude the force constant corresponding to the stretching coordinates of a given bond far exceeds the force constants that describe all the remaining interactions. Thus, in the ethane molecule the force

constant f_Q corresponding to the stretching coordinate of the C-C bond is $7.02 \cdot 10^6$ cm^{-2}, while the force constant describing the interaction of the stretching coordinates of the C-C and C-H bonds is $0.05 \cdot 10^6$ cm^{-2}, the force constant corresponding to the stretching coordinate of the C-H bond is $8.02 \cdot 10^6$ cm^{-2}, while the force constant describing the interaction of adjoining C-H bonds is $0.05 \cdot 10^6$ cm^{-2}.

It is essential to note that the force constants describing the interaction of the stretching coordinate of a given bond with the adjoining bonds are not only small in absolute magnitude, but also depend weakly on the nature of this adjoining bond /sic/. For example, the above-presented values for the force constants of the interaction of the C-H bond with the neighboring C-H bond or the neighboring C-C bond in both cases are $0.05 \cdot 10^6$ cm^{-2}. This also is true of the deformational coordinates. It should be added that in most organic compounds the angles between bonds are equal to the tetrahedral (109°28'), 120°, or close to it.

Thus, to a close enough approximation, we can represent the sum in the right-hand side of Eq. (II.13) as a series of subsums, each of which contains the elements $\{G\}$ and $\{F\}$, corresponding to the given bond:

$$\sum_i^n \Delta\lambda \approx \sum_{im} [\{G\}_{im} - \{G^*\}_{im}] \{F\}_{im} + \sum_{il} [\{G\}_{il} - \{G^*\}_{il}] \{F\}_{il} \cdots \text{ and so on.} \qquad \text{(II.14)}$$

Here the subscripts m and l correspond to the coordinate numbers, but refer to different bonds.

By entering the notation L_j' for the sum in the right-hand side of Eq. (II.14), we rewrite it in a more compact form:

$$\sum_i^n \Delta\lambda = \sum_i^m L_j', \qquad \text{(II.15)}$$

where m now is the number of bonds in a molecule and j is the bond index.

The product of the roots of the secular equation is equal to /78 the determinant of GF

$$\prod_i^n \lambda_i^* = \text{Det GF}. \qquad \text{(II.16)}$$

Similarly, for the isotopic species:

$$\prod_i^n \lambda_i^* = \mathrm{Det}\,\mathbf{G}^*\mathbf{F}, \tag{II.17}$$

where the elements of the **F**-matrix in both cases are equal. Hence

$$\prod_i^n \frac{\lambda_i^*}{\lambda_i} = \frac{\mathrm{Det}\,\mathbf{G}^*}{\mathrm{Det}\,\mathbf{G}}. \tag{II.18}$$

If the force constants are expressed in units of 10^6 cm^{-2}, the roots of the secular equation are equal to the squares of the corresponding frequencies:

$$\lambda_i = \tilde{\nu}_i^2 \tag{II.19}$$

and in view of the fact that $\Delta\lambda \ll \lambda$,

$$\Delta\lambda_i = 2\Delta\nu_i. \tag{II.20}$$

Therefore,

$$\sum_i^n \Delta\tilde{\nu}_i = \frac{1}{2}\sum_i^n \Delta\lambda_i = \frac{1}{2}\sum_j^m L_j' \tag{II.21}$$

and with reference to Eqs. (II.18) and (II.19)

$$\prod_i^n \frac{\tilde{\nu}_i^*}{\nu_i} = \frac{\sqrt{\mathrm{Det}\,\mathbf{G}^*}}{\sqrt{\mathrm{Det}\,\mathbf{G}}}. \tag{II.22}$$

Substituting Eqs. (II.21) and (II.22) into Eq. (II.5), we get: /79

$$\beta = \sqrt{\frac{\mathrm{Det}\,\mathbf{G}^*}{\mathrm{Det}\,\mathbf{G}}}\left(1 + \frac{a}{2}\sum_j^m L_j'\right). \tag{II.23}$$

The ratio of the determinants of matrices **G*** and **G** appearing ahead of the parentheses in the right-hand is always less than unity, and it differs little from unity, therefore it can be represented as

$$\frac{\mathrm{Det}\,\mathbf{G}^*}{\mathrm{Det}\,\mathbf{G}} = 1 - d. \tag{II.24}$$

Then

$$\beta \approx \left(1-\frac{d}{2}\right)\left(1+\frac{a}{2}\sum_{i}^{m} L_j^*\right). \qquad \text{(II.25)}$$

Since both parenthetical expressions in the right-hand side are close to unity in order of magnitude, the β-factor can be represented in the following notation:

$$\beta \approx 1+\frac{a}{2}\sum_{i}^{m} L_j^* - \frac{d}{2}. \qquad \text{(II.26)}$$

Finally, introducing the notation $\frac{a}{2}L_j^* = L_j$ and $-\frac{d}{2} = \Delta$, we get

$$\beta = 1+\sum_{j}^{m} L_j + \Delta, \qquad \text{(II.27)}$$

where L_j is the isotopic bond number and Δ is the structure correction.

Eq. (II.27) in form is analogous to Eq. (II.1), which confirms the physical soundness of the approach that was taken as the basis for finding the β-factors in terms of isotopic bond numbers.

Satisfactory agreement of the β-factors calculated in terms of the frequencies of vibrations and in terms of the bond numbers sets up a basis for estimating β-factors of as yet uninvestigated carbon compounds.

Table 28 gives the values of β-factors obtained by using isotopic bond numbers.

Isotopic Equilibrium of Carbon in Biological Systems /90

The question can arise as to whether there is any physical significance of the β-factors obtained by calculation and the partition coefficients of high-molecular compounds, bearing in mind that these parameters characterize isotope fractionation at the state of equilibrium of isotope exchange, while it is wholly clear that the attainment of equilibrium in systems that are so high in molecular weight in most cases is an improbable event.

TABLE 28. THERMODYNAMIC ISOTOPIC FACTORS FOR ORGANIC COMPOUNDS CALCULATED BY THE ISOTOPIC BOND NUMBER METHOD

Compound	Structural formula	Notation of β factors	Set of isotopic bond numbers	β_r-factors	β_Σ-factors
1	2	3	4	5	6
Isobutane	$CH_3\overset{3}{\underset{}{\vert}}$ $CH_3{-}\overset{1}{C}\overset{2}{H}{-}\overset{4}{C}H_3$	$\beta_{1,3,4}$ β_2	$3L_{C-H}$, L_{C-C} L_{C-H}, L_{C-C}	1.131 1.167	1.140
Isopentane	$CH_3\overset{5}{\underset{}{\vert}}$ $CH_3{-}\overset{1}{C}\overset{2}{H}{-}\overset{3}{C}H_2{-}\overset{4}{C}H_3$	$\beta_{1,4,5}$ β_2 β_3	$3L_{C-H}$, L_{C-C} L_{C-H}, $3L_{C-C}$ $2L_{C-H}$, $2L_{C-C}$	1.131 1.167 1.149	1.142
Neopentane	$CH_3\overset{3}{\underset{}{\vert}}$ $CH_3{-}\overset{1}{\underset{\vert}{C}}\overset{2}{\underset{\vert}{}}{-}\overset{4}{C}H_3$ $CH_3\overset{5}{\underset{}{\vert}}$	$\beta_{1,3,4,5}$ β_2	$3L_{C-H}$, L_{C-C} $_4L_{C-C}$	1.131 1.184	1.142
Ethylene	$\overset{1}{C}H_2{=}\overset{2}{C}H_2$	$\beta_{1,2}$	$2L_{C-H}$, $L_{C=C}$	1.135	1.135
Acetylene	$\overset{1}{C}H{\equiv}\overset{2}{C}H$	$\beta_{1,2}$	L_{C-H}, L_{C-C}	1.117	1.117
Divinyl	$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2$	$\beta_{1,4}$ $\beta_{2,3}$	$2L_{C-H}$, $L_{C=C}$ L_{C-H}, L_{C-C}, $L_{C=C}$	1.135 1.153	1.144

TABLE 28 /continued/

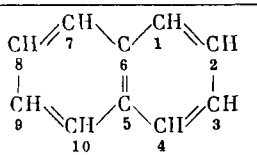
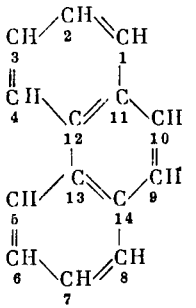
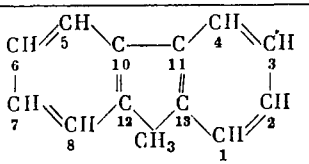
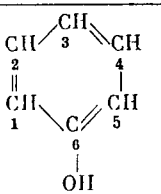
Compound	Structural formula	Notation of β-factors	Set of isotopic bond numbers	β_1-factors	β-factors
Butyne	$CH_3-C\equiv C-CH_3$ (1 2 3 4)	$\beta_{1,4}$ $\beta_{2,3}$	$3L_{C-H}$, L_{C-C} L_{C-C}, $L_{C\equiv C}$	1.131 1.134	1.133
Naphthalene		$\beta_{1-4,\ 7-10}$ $\beta_{5,\ 6}$	$2L_{C\equiv C}$, L_{C-H} $2L_{C-C}$, $L_{C=C}$	1.153 1.170	1.156
Phenanthrene		β_{1-10} β_{11-14}	L_{C-H}, $2L_{C\equiv C}$ $2L_{C-C}$, $L_{C=C}$	1.153 1.170	1.158
Fluorene		β_{1-8} β_{10-13} β_9	L_{C-H}, $2L_{C\equiv C}$ $2L_{C-C}$, $L_{C=C}$ $2L_{C-H}$, $2L_{C-C}$	1.153 1.170	1.159
Phenol		β_{1-5} β_6	$2L_{C\equiv C}$, L_{C-H} L_{C-C}, $L_{C=C}$, L_{C-O}	1.153 1.179	1.157

TABLE 28 /continued/

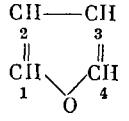
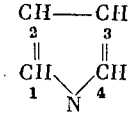
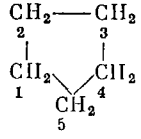
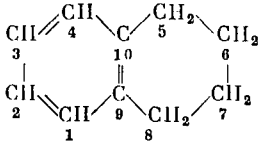
Compound	Structural formula	Notation of β-factors	Set of isotopic bond numbers	β_i-factors	β-factors
1	2	3	4	5	6
Furan		$\beta_{1,4}$ $\beta_{2,3}$	L_{C-H}, L_{C-O}, L_{C-C} L_{C-H}, L_{C-C}, $L_{C=C}$	1.161 1.153	1.157
Pyrrole		$\beta_{1,4}$ $\beta_{2,3}$	L_{C-H}, L_{C-N}, $L_{C=C}$ L_{C-H}, L_{C-C}, $L_{C=C}$	1.159 1.153	1.156
Cyclobenzene		β_{1-5}	$2L_{C-H}$, $2L_{C-C}$	1.149	1.149
Tetralin		β_{1-4} β_{5-8} β_{9-10}	L_{C-H}, L_{C-C}, $L_{C=C}$ $2L_{C-H}$ $2L_{C-C}$ $2L_{C-C}$, $L_{C=C}$	1.153 1.149 1.170	1.157

TABLE 28 /continued/

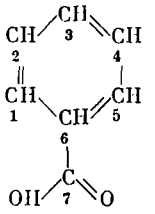
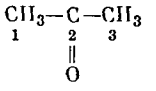
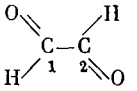
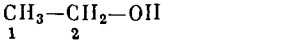
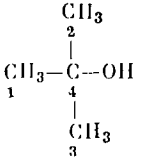
Compound	Structural formula	Notation of β factors	Set of isotopic bond numbers	β_1-factors	β-factors
Benzoic acid		$\beta_{1,2,3,4,5}$ β_6 β_7	L_{C-H}, $2L_{C=C}$ $2L_{C=C}$, L_{C-C} L_{C-C}, L_{C-O}, $L_{C=O}$	1.153 1.170 1.197	1.188
Acetone		$\beta_{1,3}$ β_2	$3L_{C-H}$, L_{C-C} $2L_{C-C}$, $L_{C=O}$	1.131 1.188	1.150
Glyoxal		$\beta_{1,2}$	L_{C-H}, L_{C-C}, $L_{C=O}$	1.171	1.171
Ethyl alcohol		β_1 β_2	$3L_{C-H}$, L_{C-C} $2L_{C-H}$, L_{C-C}, L_{C-O}	1.131 1.158	1.144
Tertiary butyl alcohol		$\beta_{1,2,3}$ β_4	$3L_{C-H}$, L_{C-C} $3L_{C-C}$, L_{C-O}	1.131 1.193	1.147

TABLE 28 /continued/

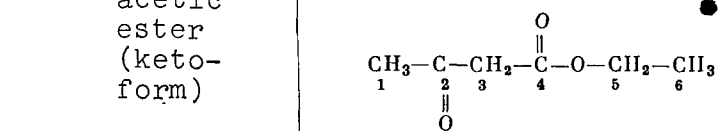
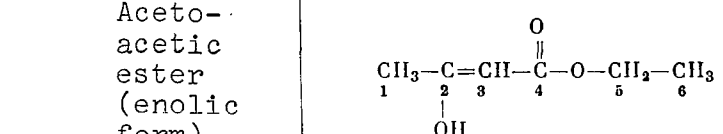
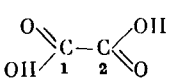
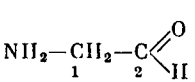
Compound	Structural formula	Notation of β-factors	Set of isotopic bond numbers	β_i-factors	β-factors
1	2	3	4	5	6
Acetoacetic ester (ketoform)		β_1	$3L_{C-H}$, L_{C-C}	1.131	1.159
		β_2	$2L_{C-C}$, $L_{C=O}$	1.188	
		β_3	$2L_{C-H}$, $2L_{C-C}$	1.149	
		β_4	L_{C-C}, L_{C-O}, L_{C-O}	1.197	
		β_5	$2L_{C-H}$, L_{C-C}, L_{C-O}	1.158	
		β_6	$3L_{C-H}$, L_{C-C}	1.131	
Acetoacetic ester (enolic form)		β_1	$3L_{C-H}$, L_{C-C}	1.131	1.161
		β_2	L_{C-C}, L_{C-O}, $L_{C=C}$	1.197	
		β_3	L_{C-H}, L_{C-C}, $L_{C=C}$	1.150	
		β_4	L_{C-C}, $L_{C=O}$, L_{C-O}	1.197	
		β_5	$2L_{C-H}$, L_{C-C}, L_{C-O}	1.158	
		β_6	$3L_{C-H}$, L_{C-C}	1.131	
Oxalic acid		$\beta_{1,2}$	L_{C-C}, L_{C-O}, $L_{C=O}$	1.197	1.197
Glycine (glycocol)		β_1	$2L_{C-H}$, L_{C-C}, L_{C-N}	1.155	1.176
		β_2	L_{C-H}, L_{C-C}, $L_{C=O}$	1.197	

TABLE 28 /continued/

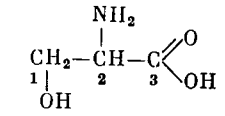
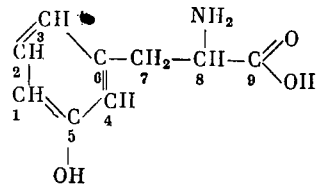
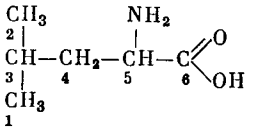
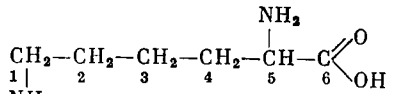
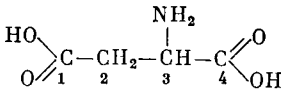
Compound	Structural formula	Notation of β-factors	Set of isotopic bond numbers	β_1-factors	β-factors
Serine		β_1	$2L_{C-H}$, L_{C-C}, L_{C-O}	1.158	1.176
		β_2	L_{C-H}, L_{C-C}, L_{C-N}	1.173	
		β_3	L_{C-C}, L_{C-O}, $L_{C=O}$	1.197	
Tyrosine		β_{1-4}	L_{C-H}, $2L_{C=C}$	1.153	1.164
		β_5	L_{C-O}, $2L_{C=C}$	1.179	
		β_6	L_{C-C}, $2L_{C=C}$	1.170	
		β_7	$2L_{C-H}$, $2L_{C-C}$	1.149	
		β_8	L_{C-H}, $2L_{C-C}$, L_{C-N}	1.173	
		β_9	L_{C-C}, L_{C-O}, $L_{C=O}$	1.197	
Leucine		$\beta_{1,2}$	$3L_{C-H}$, L_{C-C}	1.131	1.158
		β_3	L_{C-H}, $3L_{C-C}$	1.167	
		β_4	$3L_{C-H}$, $2L_{C-C}$	1.149	
		β_5	L_{C-H}, $2L_{C-C}$, L_{C-N}	1.173	
		β_6	L_{C-H}, L_{C-O}, $L_{C=O}$	1.197	
Lysine		β_1	$2L_{C-H}$, L_{C-C}, L_{C-N}	1.155	1.162
		$\beta_{2,3,4}$	$2L_{C-H}$, $2L_{C-C}$	1.149	
		β_5	L_{C-H}, $2L_{C-C}$, L_{C-N}	1.173	
		β_6	L_{C-C}, L_{C-O}, $L_{C=O}$	1.197	
Aspargic acid		$\beta_{1,4}$	L_{C-C}, L_{C-O}, $L_{C=O}$	1.197	1.179
		β_2	$2L_{C-H}$, $2L_{C-C}$	1.149	
		β_3	L_{C-H}, $2L_{C-C}$, L_{C-N}	1.173	

TABLE 28 /continued/

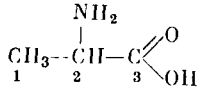
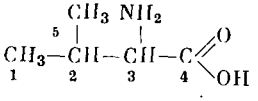
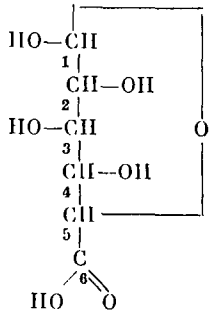
Compound	Structural formula	Notation of β-factors	Set of isotopic bond numbers	β_1-factors	β-factors
1	2	3	4	5	6
α- Alanine		β_1	$3L_{C-H}$, L_{C-C}	1.131	1.167
		β_2	L_{C-H}, $2L_{C-C}$, L_{C-N}	1.173	
		β_3	L_{C-C}, L_{C-O}, $L_{C=O}$	1.197	
Valine		$\beta_{1,5}$	$3L_{C-H}$, L_{C-C}	1.131	1.159
		β_2	L_{C-H}, $3L_{C-C}$	1.167	
		β_3	L_{C-H}, $2L_{C-C}$, L_{C-N}	1.171	
		β_4	L_{C-C}, L_{C-O}, $L_{C=O}$	1.197	
Hemicellulose, β-D-glucoronic acid		β_1	L_{C-H}, L_{C-C}, $2L_{C-O}$	1.185	1.181
		$\beta_{2,4}$	L_{C-H}, $2L_{C-C}$, L_{C-O}	1.176	
		β_3	L_{C-H}, $2L_{C-C}$, L_{C-O}	1.176	
		β_5	L_{C-H}, $2L_{C-C}$, L_{C-O}	1.176	
		β_6	L_{C-C}, $L_{C=O}$, L_{C-O}	1.197	

TABLE 28 /continued/

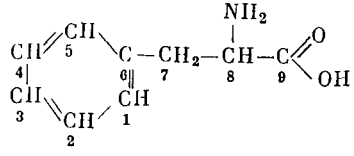
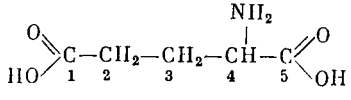
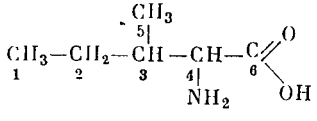
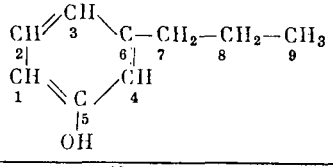
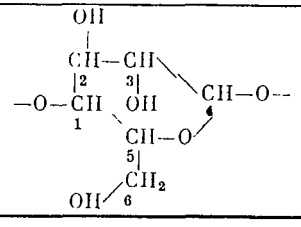
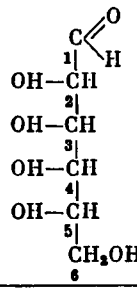
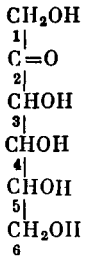
Compound	Structural formula	Notation of β-factors	Set of isotopic bond numbers	β_i-factors	β-factors
Phenylalanine		$\beta_{1,2,3,4,5}$	L_{C-H}, $2L_{C=C}$	1.153	
		β_6	L_{C-C}, $2L_{C=C}$	1.170	
		β_7	$2L_{C-H}$, $2L_{C-C}$	1.149	1.162
		β_8	L_{C-H}, $2L_{C-C}$, L_{C-N}	1.176	
		β_9	L_{C-C}, L_{C-O}, $L_{C=O}$	1.197	
Glutamic acid		$\beta_{1,5}$	L_{C-C}, L_{C-O}, $L_{C=O}$	1.197	
		β_2	$2L_{C-H}$, $2L_{C-C}$	1.149	1.173
		β_3	$2L_{C-H}$, $2L_{C-C}$	1.149	
		β_4	L_{C-H}, $2L_{C-C}$, L_{C-N}	1.173	
Isoleucine		β_1	$3L_{C-H}$, L_{C-C}	1.131	
		β_2	$2L_{C-H}$, $2L_{C-C}$	1.149	
		β_3	L_{C-H}, $3L_{C-C}$	1.167	
		β_4	L_{C-H}, $2L_{C-C}$, L_{C-N}	1.173	1.158
		β_5	$3L_{C-H}$, L_{C-C}	1.131	
		β_6	L_{C-H}, L_{C-O}, $L_{C=O}$	1.197	
n-Hydroxyphenylpropane		β_{1-4}	L_{C-H}, $2L_{C-C}$	1.153	
		β_5	$2L_{C-C}$, L_{C-O}	1.179	
		β_6	L_{C-C}, $2L_{C-C}$	1.170	1.154
		$\beta_{7,8}$	$2L_{C-H}$, $2L_{C-C}$	1.149	
		β_9	L_{C-C}, $3L_{C-H}$	1.131	
Monomeric unit of cellulose		$\beta_{1,2,3,5}$	L_{C-H}, $2L_{C-C}$, L_{C-O}	1.176	
		β_4	L_{C-H}, L_{C-C}, $2L_{C-O}$	1.185	1.174
		β_6	$2L_{C-H}$, L_{C-C}, L_{C-O}	1.158	

TABLE 28 /continued/

Compound	Structural formula	Notation of β-factors	Set of isotopic bond numbers	β_1-factors	β-factors
1	2	3	4	5	6
Palmitic acid	$\overset{1}{CH_3}-\overset{2-15}{(CH_2)_{14}}-\overset{16}{C}(=O)-\overset{}{OH}$	β_1 β_{2-15} β_{16}	$3L_{C-H}$, L_{C-C} $2L_{C-H}$, $2L_{C-C}$ L_{C-C}, L_{C-O}, $L_{C=O}$	1.131 1.149 1.197	1.150
Oleic acid	$\overset{1}{CH_3}-\overset{2-15}{(CH_2)_{14}}-\overset{16}{(CH}=\overset{17}{CH})-\overset{18}{C}(=O)-OH$	β_1 β_{2-15} $\beta_{16,17}$ β_{18}	$3L_{C-H}$, L_{C-C} $2L_{C-H}$, $2L_{C-C}$ L_{C-H}, L_{C-C}, $L_{C=C}$ L_{C-H}, L_{C-O}, $L_{C=O}$	1.131 1.149 1.153 1.197	1.150
Linoleic acid	$\overset{1}{CH_3}-\overset{2-11}{(CH_2)_{10}}-\overset{12-17}{(CH}=CH)_3-\overset{18}{C}(=O)-OH$	β_1 β_{2-11} β_{12-17} β_{18}	$3L_{C-H}$, L_{C-C} $2L_{C-H}$, $2L_{C-C}$ $2L_{C-H}$, L_{C-C}, $L_{C=C}$ L_{C-C}, L_{C-O}, $L_{C=O}$	1.131 1.149 1.153 1.197	1.152
Linolic acid	$\overset{1}{CH_3}-\overset{2-13}{(CH_2)_{12}}-\overset{14-17}{(CH}=CH)_2-\overset{18}{C}(=O)-OH$	β_1 β_{2-13} β_{14-17} β_{18}	$3L_{C-H}$, L_{C-C} $2L_{C-H}$, $2L_{C-C}$ L_{C-H}, L_{C-C}, $L_{C=C}$ L_{C-C}, L_{C-O}, $L_{C=O}$	1.131 1.149 1.153 1.197	1.151

TABLE 28 /concluded/

Compound	Structural formula	Notation of β-factors	Set of isotopic bond numbers	β_i-factors	β-factors
Glucose		β_1	L_{C-H}, L_{C-C}, $L_{C=O}$	1.169	
		β_{2-5}	L_{C-H}, $2L_{C-C}$, L_{C-O}	1.175	1.171
		β_6	$2L_{C-H}$, L_{C-C}, L_{C-O}	1.158	
Fructose		$\beta_{1,6}$	$2L_{C-H}$, L_{C-C}, L_{C-O}	1.158	
		β_2	$2L_{C-C}$, $L_{C=O}$	1.187	1.171
		β_{3-5}	$2L_{C-C}$, L_{C-H}, L_{C-O}	1.175	
Porphyrin ring of chlorophyll	Shown in Fig. 74	$\beta_{23,26,28,29,32}$	$3L_{C-H}$, L_{C-C}	1.131	
		$\beta_{27,30,31}$	$2L_{C-H}$, $2L_{C-C}$	1.149	
		β_{25}	$2L_{C-H}$, $L_{C=C}$	1.135	
		$\beta_{1,4,7,24}$	L_{C-H}, L_{C-C}, $L_{C=C}$	1.153	
		β_{20-22}	L_{C-H}, $3L_{C-C}$	1.167	
		$\beta_{10,13-18}$	$2L_{C-C}$, $L_{C=C}$	1.170	1.162
		$\beta_{3,5,6,8,11,12}$	L_{C-C}, $L_{C=C}$, L_{C-N}	1.176	
		$\beta_{2,9}$	$2L_{C-C}$, $L_{C=N}$	1.174	
		β_{19}	$2L_{C-C}$, $L_{C=O}$	1.188	
		$\beta_{33,35}$	L_{C-C}, L_{C-O}, $L_{C=O}$	1.196	
		β_{34}	$3L_{C-H}$, L_{C-O}	1.140	
Phytol of chlorophyll	$-O-C_{19}H_{36}-CH_3$	—	—	—	1.150

In this respect, it is appropriate to present some considerations. Evidently, one must differentiate between primary and secondary thermodynamic isotope effects. Primary thermodynamic isotope effects are responsible for the distribution of isotopes in the components of a system if these components are formed in a single process, as well as the intramolecular distribution of isotopes in a polyatomic compound at the instant of its formation. In other words, primary thermodynamic isotope effects are always associated with chemical transformations of matter. In contrast to this, the redistribution of isotopes resulting from specifically isotope exchange reactions not accompanied by chemical change of the material is associated with secondary isotope effects.

Let us take, for example, the system CO_2 - CH_4 playing a major role in the geochemistry of carbon isotopes. Methane and carbon dioxide are present at the same time in natural gases of sedimentary rocks and in volcanic gases. Under certain conditions, exchange between these compounds leads to the redistribution of carbon isotopes, that is, to a secondary thermodynamic isotope effect. However, the isotope exchange of carbon in the system CO_2 - CH_4 begins to be manifested at a temperature not lower than 150-200° C. At 25° C, isotope equilibrium, as we have shown in our study of gaseous inclusions in minerals /47/ is not attained even over protracted geologic time (400 million years).

The same constituents can be formed at the same time at low temperatures, for example, in the microbiological fermentation of acetic acid. At temperatures of 25-30° C, this process yields a distribution coefficient of carbon isotopes estimated by $\Delta C^{13} = 1 + (\delta C^{13}_{CO_2} - \delta C^{13}_{CH_4}) \cdot 10^2 \simeq 1{,}070$, comparable with the partition coefficient $\alpha_{300^\circ K}$ at the equilibrium of the isotope exchange CO_2 - CH_4, equal to 1.061.

Thus, if these compounds are formed as syngenetic products of the same reaction, in the transitional process there is a redistribution of isotopes in accordance with the thermodynamic isotopic factors. After these products have formed, the isotope exchange between them in most cases (at least in respect to organic compounds)virtually does not occur.

In general, the isotope exchange of carbon, with few exceptions, proceeds very slowly in the temperature range characteristic of the zone of the upper geospheres and biosphere. However, accumulated reports on the abundance of carbon isotopes, in conjunction with theoretical values obtained for thermodynamic isotopic factors lead to a conclusion that can be unexpected: most natural compounds have an isotopic composition comparable with their isotopic thermodynamic factors. /91

P. Abelson and T. Hoering /115/ studied a distribution of carbon isotopes in several constituents of photosynthesizing organisms. They established that individual amino acids in several cases exhibit a characteristic isotopic composition. Thus, leucine in various organisms is the isotopically lightest amino acid, while glutamic and aspargic acids as a rule are enriched in the heavy isotope. Table 29 gives the isotopic composition of carbon in chlorella amino acid after P. Abelson and T. Hoering and the β_{Σ}-factor calculated for the corresponding aminoacid by the above-presented method of totaling isotopic bond numbers.

It can easily be noted that corresponding to the isotopically lightest aminoacid (leucine) is a minimum value of the β-factor, that is, the enrichment of the carbon in this amino acid in C^{12} is predicted thermodynamically. The largest thermodynamic isotopic factor (β_{Σ} = 1.179) was obtained for aspargic acid, which must correspond to its highest enrichment in C^{13} at equilibrium. A correlation also holds for other amino acids (Fig. 19).

TABLE 29. COMPARISON OF ISOTOPIC COMPOSITION OF CARBON IN AMINO-ACIDS WITH CALCULATED THERMODYNAMIC ISOTOPIC FACTORS

Amino Acid	Mean content in plankton, weight %	δC^{13}, ‰	β_{Σ}-Factor
Glucine (Glu)	15.9	−1.87	1.173
Aspargine (asp)	11.5	−0.66	1.179
Serine (Ser)	6.1	−1.47	1.176
Glucine (Glu)	15.9	−1.02	1.176
Alanine (Ala)	10.5	−1.03	1.167
Tyrosine (Tyr)	2.6	−1.98	1.164
Phenylalanine (Phe)	3.4	−2.12	1.162
Leucine (Leu)	7.6	−2.27	1.158
Isoleucine (i-Leu)	3.3	−1.96	1.158
Lysine (Lys)	2.5	−1.70	1.162

P. Parker /207/ measured the isotopic composition of several individual fatty acids isolated from algae. The fatty acids in all cases were noticeably enriched in the light carbon isotope compared with the mean carbon of the biomass. However, virtually no isotopic compositional differences were detected between individual fatty acids. In Clorella pyrenoidose and Ulva sp., the isotopic composition of saturated and unsaturated fatty acids

proved to be identical within the limits of a measurement error. In the sea grass Thalassia sp., along with the general essential enrichment of fatty acids in C^{12} compared with the total plant carbon, the differentiation in isotopic composition of individual fatty acids is barely noticeable (Table 30). This distribution of carbon isotopes remarkably agrees with the very similar values of the β-factors of these fatty acids studied. Thermodynamic isotopic factors of saturated and unsaturated fatty acids are virtually identical, in contrast to amino acids, which are characterized both by a marked difference in the isotopic composition of individual compounds, as well as by a correspondingly considerable difference in the thermodynamic isotopic factors. But the small differences that occur in the isotopic composition of fatty acids are in agreement with the corresponding small differences in the β-factors. /93

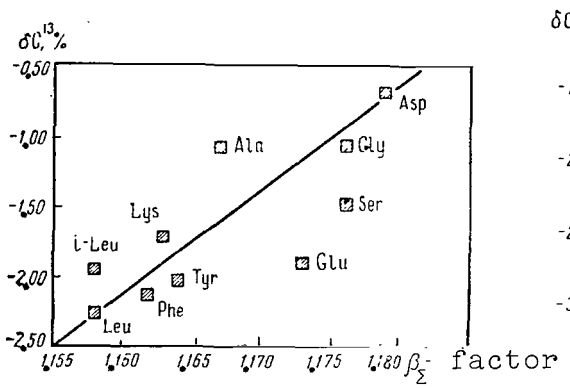
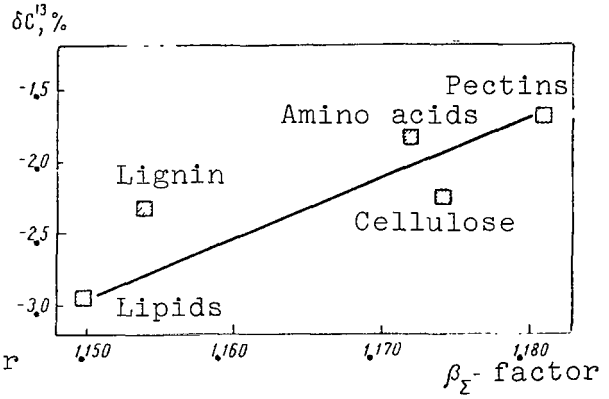


Fig. 19. Relationship between measured δC^{13} of individual amino acids in photosynthesizing organism (according to Table 29) with theoretically calculated values of thermodynamic isotopic factors (β-factors) of the corresponding amino acids.



/92

Fig. 20. Relationship of isotopic composition of carbon in biochemical constituents of plankton (according to Table 31) with calculated theoretical values of thermodynamic isotopic factors (β-factors) of the corresponding monomers.

E. Degens et al. /195/ determined not individual compounds, but individual biochemical constituents, therefore the measured value of the isotopic composition was compared with the β-factor of the compound that is most typical for the given fraction (Table 31). For example, pectin compounds have $\delta C^{13} = -1.67$ percent. Pectins are high-molecular carbohydrate compounds of acidic character, in which the principal structural unit is a segment of galacturonic acid. Accordingly, the β_Σ-factor of D-galacturonic acid was taken as the β_Σ-factor corresponding to pectins, and the results of calculating this β-factor based on the isotopic bond number method are in Table 29.

TABLE 30. COMPARISON OF ISOTOPIC COMPOSITION OF CARBON IN FATTY ACIDS WITH THEIR CALCULATED THERMODYNAMIC ISOTOPIC FACTORS

Fatty acids	δC^{13}, ‰	β_Σ- Factor
Total carbon in plant (*Thalassia sp.*)	−0.77	—
Palmitic	−2.2	1.150
Stearic	−2.15	1.150
Oleic	−2.2	1.150
Linolic	−2.2	1.151
Linoleic	−1.9	1.152

The isotopic composition of a fraction called the lignin fraction by E. Degens et al. is characterized by $\delta C^{13} = -2.31$ percent. Lignin is constructed of phenylpropane monomers. The β-factor of n-hydroxyphenylpropane ($\beta_\Sigma = 1.154$) is taken as the β-factor for lignin.

The thermodynamic isotopic factor of a typical representative of the lipids such as palmitic acid was brought into correspondence with the lipid fraction.

As the β-factor characterizing the total amino acid fraction, the mean value calculated from data for individual amino acids with reference to their abundance was used (see Table 29). The value $\beta_\Sigma = 1.172$ was obtained.

From Fig. 20 we can see the well-defined relationship between the isotopic composition of constituent carbon and the values of the β_Σ-factors characterizing them.

Since in calculating the β_Σ-factors we started from the concept of intramolecular thermodynamic isotope effects, this correspondence indicates not only the intermolecular fractionation of isotopes, but also the intramolecular isotopic nonuniformity. By the way, the latter has been established directly. P. Abelson and T. Hoering decarboxylated amino acids and measured separately the isotopic composition of the carbon in the carboxyl group and the decarboxylated residue, that is, in practice they studied the intramolecular distribution of isotopes. /95
As was established directly by quantum-statistical calculations of thermodynamic isotopic factors of acetic and formic acids, and also as follows from the procedure of summing the corresponding isotope bond numbers for the carboxyl groups of amino acids (see Table 28), a very high β_1-factor corresponds to the latter. This

means that at equilibrium carboxyl group carbon must be sharply enriched in the heavy isotope. It is precisely this that was observed by P. Abelson and T. Hoering. Fig. 21 gives a comparison of the data of these investigators with calculated values of the internal thermodynamic isotopic factors (β_i-factors) corresponding to the structural groups of the amino acids studied.

TABLE 31. COMPARISON OF ISOTOPIC COMPOSITION OF CARBON IN BIOCHEMICAL CONSTITUENTS OF MARINE PLANKTON WITH THERMODYNAMIC ISOTOPIC FACTORS OF THE MOST COMMON STRUCTURAL ELEMENTS OF THE CORRESPONDING CONSTITUENTS /94

Biochemical fraction	δC^{13}, %	Compound, β_Σ-factor of which is calc'd	β_Σ-Factor
Lipids (chloroform-extracted)	−2.98	Palmitic acid	1.150
Pectins	−1.67	*D*-galacturonic acid	1.181
Cellulose	−2.24	Cellulose (monomer)	1.174
Amino acids	−1.75	Amino acids	1.72 (mean value)
Lignin	−2.31	n-Hydroxyphenylpropane	1.154

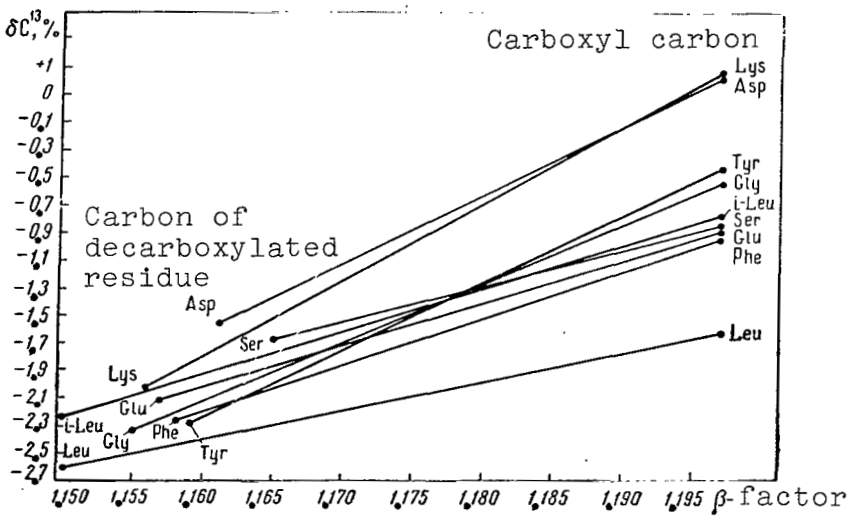


Fig. 21. Relationship of measured values of the isotopic composition of carbon in structural fragments of amino acids with the theoretically calculated values of the thermodynamic isotopic factors.

Thus, it became clear that the distribution of carbon isotopes in biochemical fractions of organic matter is regulated by the values of the β_i-factors and the β_Σ-factors, that is, by the intramolecular and intermolecular thermodynamic isotope effects. But thermodynamic isotope effects characterize the distribution of isotopes in isotope exchange equilibrium. Therefore we arrive at the fundamental conclusion that carbon undergoes isotopic equilibrium in biological systems.

This conclusion can raise some skepticism. The view is held that no system is so far removed from the equilibrium state as biological systems. Moreover, isotope exchange of carbon between organic compounds occurs extremely slowly. Below we present the results of our experiments with the isotope exchange of carbon in hydrocarbon systems, from which it follows that reaching isotope exchange equilibrium in these systems even at 300° C requires a period of time reckoned in the millions of years. However, there are reports that during chemical transformations very rapid exchange can occur if intermediate labile species are formed, whose lifetime exceeds the theory of thermal vibrations, that is, $10^{-10} - 10^{-12}$ sec. For example, they include free radicals, which in all probability have a leading role in biosynthesis.

In organic systems isotopic exchange can be carried out through a common donor. S. Z. Roginskiy, for example, points out that exchange of Br between organic bromides does not occur, but each of them easily exchanges Br with aluminum bromide, as a result of which the distribution of bromine isotopes between organic bromides must correspond to the equilibrium constant of their isotopic exchange /103/. Possibly, a similar type of conjugate isotopic exchange reaction occurs in biological systems, where enzyme carbon plays the role of common donor.

Thermodynamic isotopic factors determine the maximum values /96
of the possible intramolecular isotopic nonuniformity attained in the limiting case of exchange isotopic equilibrium. In practice, intramolecular isotope effects evidently must be smaller.

By comparing the actual isotopic shift $\Delta C^{13}_{meas} = \delta C^{13}_{AX_n} - \delta C^{13}_{BX_m}$ with the equilibrium values $C^{13}_{theor} = (\alpha - 1)\cdot 10^2$, determined by the ratio of thermodynamic isotope factors $(\alpha = \beta_{\Sigma_{AX_n}}/\beta_{\Sigma_{BX_m}})$, we can arrive at the concept of the coefficient of biochemical equilibrium (let us denote it with $\chi = \Delta C^{13}_{meas}/\Delta C^{13}_{theor}$), that is, we can estimate the degree of attainment of isotopic equilibrium in biological systems. This can easily be done by inspecting the graphs given in Figs. 19-21.

As is clear from Fig. 19, the coefficient of biochemical isotopic equilibrium $\kappa = 0.8$ for individual amino acids. Inter-constituent fractionation of isotopes (see Fig. 20) is characterized by $\kappa = 0.42$. The degree of attainment of intramolecular isotopic equilibrium between carboxyl group carbon and the mean carbon of the rest of the molecule can on the average be determined by $\kappa = 0.55$, where for some amino acids this quantity varies from 0.32 to 0.80.

Thus, we are speaking not only about some tendency in the distribution of carbon isotopes in biochemical constituents that are in correspondence with the correlations of the distribution of their thermodynamic isotopic factors. There exists a fairly close mutually unique correspondence between the theoretical and the measured isotopic shifts, which indicates a relatively high degree of attainment of isotopic equilibrium in biological systems. Deviation of isotopic shifts from equilibrium values in this case is capable, as we can easily understand, of conveying information about the features of the biological process.

Moreover, in this study we will not delve into a discussion of the mechanism of this phenomenon, since the concepts and information presented in the first chapters are necessary only as a basis for dealing with questions touching on the geochemistry and geology of petroleum and gas. From this point of view, the only important thing is that there is the fact of intramolecular isotopic nonuniformity in biological systems and that this phenomenon can be studied with the apparatus of isotope thermodynamics.

Intramolecular Isotopic Nonuniformity

In the light of the foregoing, the equilibrium distribution of isotopes by isotopic species of polyatomic compounds is a reality in the biological systems of organisms and in their metabolic products.

Polyatomic molecules containing exchange-nonequivalent /97
atoms of a given element are not only theoretically characterized by intramolecular isotope effects, but the latter are realized in the form of the isotopic nonuniformity of the biological constituents. It must be stressed that the "intramolecular" concept bears a purely statistical significance (that is, it refers not to a single molecule, but to their ensembles) and only in this sense can we pass from the concept of the β-factor as a parameter of an isotopic species substituted at a given atom to the β-factor as a parameter characterizing isotopic properties of the atom in a given position.

The value of the thermodynamic intramolecular isotope effect must obviously be expressed by the ratio of the β-factors of the isotopic species of the given compound. Here it is necessary that this quantity (let us call it α_i) be measurable, like the thermodynamic isotope effect α characterizing the separation of isotopes in a system.

The following determination of α_i satisfies this condition:

$$\alpha_i = \frac{\beta_\Sigma}{\frac{1}{k}\sum_i^k \beta_i}. \qquad \text{(II.28)}$$

In this case α_i refers to a bond and determines the difference between the isotopic composition of the fragment cleaving upon dissociation at the given bond from the isotopic composition of the initial compound (without allowance for the kinetic isotope effect). Here k is the number of atoms in the isolated fragment.

In several cases it is convenient to express the internal thermodynamic isotopic effect by the ratio of the isotopic compositions of the fragments into which the molecule breaks down when a given bond is broken:

$$\alpha_i' = \frac{\frac{1}{n-k}\sum_{k+1}^n \beta_i}{\frac{1}{k}\sum_i^k \beta_i}. \qquad \text{(II.29)}$$

We can establish a relationship between the quantities α_i and α_i'. Let us represent Eq. (II.28) as follows:

$$\alpha_i = \frac{\frac{1}{n}\left(\sum_i^k \beta_i + \sum_{k+1}^n \beta_i\right)}{\frac{1}{k}\sum_i^k \beta_i}. \qquad \text{(II.30)}$$

By solving Eq. (II.29) for the quantity $\sum_{k+1}^n \beta_i$ and by substituting into Eq. (II.30), we get: /98

$$\alpha_i = \frac{\frac{1}{n}\left(\sum_i^k \beta_i + \alpha_i \frac{(n-k)}{k}\sum_i^k \beta_i\right)}{\frac{1}{k}\sum_i^k \beta_i}. \qquad \text{(II.31)}$$

After canceling out and transformations, we have

$$\alpha_i' = \frac{k}{n-k}\left(\frac{n}{k}\alpha_i - 1\right). \qquad \text{(II.32)}$$

For example, the intramolecular thermodynamic isotope effect of pentane α_1 with respect to the C_1-C_2 bond at 300° K, under Eq. (II.28) and Table 7, is 1.0095, while according to Eq. (II.29) α_1' = 1.0119. Since $\alpha_i > 1$, the cleaved group is enriched in the light isotope compared with the initial carbon.

It should be noted that estimating the intramolecular effect from the ratio of the β_i-factors characterizing atoms on both sides of the broken bond, β_k and β_{k+1}, is not expedient, since this ratio does not correspond to any experimentally measurable quantity.

The existence of nonequivalent atoms is responsible for the isotopic nonuniformity of the compound. A measure of this nonuniformity can be established thusly. The thermodynamic isotopic factor of a compound -- β_Σ -- in the general case is larger than the β-factor of a wholly isotopically replaced species β_n.

Actually, by definition

$$\beta_\Sigma = \frac{1}{n}\sum_i^n \beta_i \quad \text{и} \quad \beta_n = \left(\prod_i^n \beta_i\right)^{\frac{1}{n}}, \qquad \text{(II.33)}$$

and therefore by the familiar rule $\frac{a+b+\ldots+c}{n} \geqslant \sqrt[n]{abc}$

$$\beta_\Sigma \geqslant \beta_n. \qquad \text{(II.34)}$$

Equality is attained if the β_q-factors of all the isotopic species are equal, that is, the molecule is thermodynamically isotopically homogeneous. In contrast, if the thermodynamic isotopic factors are too similar, then inequality (II.34) is satisfied, and the larger the difference in the values of β_q, the stronger the inequality. Thus, the ratio of the β_Σ-factor to its value for the wholly isotopically-replaced species can serve as a measure of the internal isotopic nonuniformity ψ of the molecule:

$$\xi = \frac{\beta_\Sigma}{\beta_n}. \qquad \text{(II.35)}$$

TABLE 32. COEFFICIENTS OF ISOTOPIC NONUNIFORMITY ψ OF NORMAL ALKANES /99

T, K	C_3H_8	C_4H_{10}	C_5H_{12}
100	1,0005054	1,0006773	1,0006999
200	1,0000825	1,0001115	1,0001278
300	1,0000232	1,0000297	1,0000306
400	1,0000044	1,0000061	1,0000075
500	1,0000024	1,0000033	1,0000037
600	1,0000006	1,0000014	1,0000015
700	1,0000004	1,0000006	1,0000009
800	1,0000001	1,0000002	1,0000002

For CH_4, as a monoatomic compound, and C_2H_6, as a compound containing equivalent atoms $\xi = 1$ (Table 32). Isotopic nonuniformity is at a maximum in low-molecular compounds containing nonequivalent atoms. There is a temperature dependence of isotopic nonuniformity: ξ decreases with increase in temperature.

The isotopic nonuniformity of molecules caused by intramolecular isotope effects can strongly affect the distribution of isotopes in the dissociation products of the corresponding compound.

Reactions in which complex organic compounds participate usually consist in the compounds losing and adding on individual structural groups or fragments, for example, functional groups, side radicals, and so on, that is during the reaction not all the possible bonds are transformed, but as a rule the most labile. On inspecting Fig. 18 illustrating the nonuniformity in the distribution of isotopes within several molecules studied, it is easy to understand what different kinds of transformations must lead to in the sense of altering the isotopic composition of compounds. For example, $\beta_\Sigma = 1{,}178$ for acetic acid. In decarboxylation, carbon characterized by a large β_1-factor is removed. Therefore, during decarboxylation the residue (in this case a hydrocarbon radical) is enriched in the light isotope. Here is another example. From Fig. 18 it is clear that if the CH_3 group of toluene is removed, the aromatic-ring carbon on /100 the average will be enriched in the heavy isotope compared with benzene carbon. Therefore the aromatic hydrocarbons formed through cleavage of alkyl substituents will be isotopically heavier than the analogous aromatic hydrocarbon not containing substituents.

Thus, knowing the calculated values of the intramolecular isotope effects and by measuring the isotopic composition of natural compounds, in principle one can judge exactly which chemical reactions have occurred, the pathway of which mechanism, and from which initial conditions the formation of the given class of compounds was reached, for example, petroleum hydrocarbons.

The isotopic composition of the cleaved fragment is ordinarily regarded as a function of the kinetic isotope effect characterizing the breaking of the given bond. But this is so if the initial compound was isotopically uniform. But if the compound contained nonequivalent atoms, the isotopic composition of the cleaved radical depends, in addition to the kinetic isotope effect, on the intramolecular distribution of isotopes characteristic of the given compound.

The kinetic isotope effect is determined by the difference in the reaction rates of the isotopic species or, which amounts to the same thing, by the ratio of the probabilities that the initial compound will dissociate at the bond X-X and X-X*.

$$\frac{k}{k^*}=\frac{ss^{\#*}}{s^*s^{\#}}\left(\frac{\mu^*}{\mu}\right)^{\frac{1}{2}}\prod\frac{\nu_i^*\,\mathrm{sh}\,\frac{h\nu_i}{2kT}}{\nu_i\,\mathrm{sh}\,\frac{h\nu_i^*}{2kT}}\prod\frac{\nu_i^{\#}\,\mathrm{sh}\,\frac{h\nu_i^{\#*}}{2kT}}{\nu_i^{*\#}\,\mathrm{sh}\,\frac{h\nu_i^{\#}}{2kT}}, \qquad \text{(II.36)}$$

where the symbol # refers to the transient complex.

As a rule, the X-X* bond proves to be stronger.

For the case of the equiprobable distribution of isotopes there is a formula linking the kinetic isotope effect k/k* to the degree of reaction completeness f (ratio of reacted part of the initial compound to its initial concentration) and by the distribution coefficient Δ (ratio of the isotopic compositions of the product and the initial compound):

$$\frac{k}{k^*}=\frac{\ln(1-f)}{\ln(1-f\Delta)}. \qquad \text{(II.37)}$$

In an isotopically-nonuniform molecule, the concentration of isotope X* at the bond broken can be greater or less than the average for the molecule. This increase in γ, as follows from the foregoing, must be determined by the ratio

$$\gamma=\frac{2\sum_{i=1}^{n}\beta_i}{n(\beta_k+\beta_{k+1})}, \qquad \text{(II.38)}$$

where β_k and β_{k+1} pertain to the isotopic species substituted at both sides of the bond broken. /101

Through quite obvious, although cumbersome transformations that we omit here, we can arrive at an expression analogous to (II.37), but taking the internal thermodynamic isotope effects into account:

$$1+\left(\frac{k}{k^*}-1\right)\frac{2\sum_{i=1}^{n}\beta_i}{n(\beta_k+\beta_{k+1})}=\frac{\ln(1-f)}{\ln\left(1-f\Delta\frac{n\sum_{i=1}^{k}\beta_i}{k\sum_{i=1}^{n}\beta_i}\right)} \qquad \text{(II.39)}$$

or, referring to Eqs. (II.29) and (II.38), we get

$$1+\left(\frac{k}{k^*}-1\right)\gamma=\frac{\ln(1-f)}{\ln\left(1-\frac{f\Delta}{\alpha_i}\right)}. \qquad \text{(II.40)}$$

From this expression it follows that if the specifically kinetic isotope effect is absent ($k/k^* = 1$), then

$$\Delta=\alpha_i. \qquad \text{(II.41)}$$

In this case, the distribution of the isotope between the dissociation products and the initial compound is entirely determined by the corresponding internal thermodynamic isotope effect.

If $f \to 0$, that is, the measurements are conducted in the first portions of the reaction product, then

$$1+\left(\frac{k}{k^*}-1\right)\gamma\simeq\frac{\Delta}{\alpha_i}; \qquad \text{(II.42)}$$

and by denoting the left-hand side with α_K, we get the relation

$$\alpha_k\alpha_i\simeq\Delta. \qquad \text{(II.43)}$$

Therefore, in the general case (but with reference to the above-indicated approximation), isotope fractionation during a reaction is determined by multiplying the kinetic isotope effect and the internal thermodynamic isotope effect characterizing rupture at a given bond.

From the simple relation (II.43) there derives a number of consequences that are essential from the standpoint of isotope geochemistry.

If we turn to the data in Tables 15 and 26, then by using Eq. (II.28), it is not difficult to calculate that the isolation, for example, of the CH_3 group from the end of the heptane molecule gives $\alpha_{i_{300^\circ K}} = 1.0128$, in other words, the cleaved fragment is enriched, just through isotope nonuniformity without taking account of the kinetic effects, by 1.28 percent in the C^{12} isotope compared with the initial compound. Cleavage of the end group -- CH_3CH_2 -- is characterized by the effect $\alpha_{i_{300^\circ K}} = 1.0041$, that is, enrichment by 0.4 percent is observed. /102

In examples involving hydrocarbons, the internal thermodynamic isotope effect is oriented just as the kinetic effect: both factors are added together, leading to the enriching of low-molecular alkanes in the light isotope.

Cases are possible when these effects are opposite in sign. For example, an isotopic species substituted at the carboxyl-group carbon is characterized by very high values of the thermodynamic isotope factor. By analyzing Table 28, one can conclude that in high-molecular, for example, fatty acids, isotope distribution must be determined in the radical by β-factors close to the β-factors of the corresponding hydrocarbon (I.150), and in the carboxyl group by a β-factor of approximately 1.18-1.19, that is, $\alpha_i = 0.97 - 0.96$. This means that when a carboxyl group is cleaved its carbon will be enriched 3-4 percent in the heavy isotope. On the other hand, the kinetic isotope effect is oriented toward enrichment of carbon dioxide formed by cleavage of the carboxyl group, in the light isotope. Analysis of reactions of the carboxylation with enriched preparations where the intramolecular distribution did not affect the effects measured gives a kinetic isotope effect $\alpha_k \simeq 1.02$ [120]. Through the addition of the competing isotope effects, the total effect can lead to the enrichment of the cleaved fragments in the heavy isotope counter to the kinetic isotope effect.

Let us look at one more aspect of the intramolecular distribution of isotopes that can be of considerable practical significance. Above it was noted that intramolecular isotope effects reflect the conditions in which a compound was formed. If subsequently this state is retarded, that is, secondary thermodynamic isotope effects do not occur to the time in which the compound exists, a situation is possible in which the same compound can have a different degree of isotopic nonuniformity, depending on the conditions in which it was formed. Here the mean isotopic composition of the compounds can be the same.

Let us clarify this with an example. Suppose that the same initial carbon could be transferred to some organic compound at 300° K, for example, with the aid of enzymes, and that the same products could be obtained at 1500° K. If we had a 100 percent yield, then in either case we would get a compound with the same isotopic composition, but with different intramolecular isotope distribution. If they are subjected to cracking by the same method (a method that in the best of cases does not require an increase in temperature, for example, by radio- or photodissociation), the isotopic composition of the dissociation products of both compounds will be dissimilar. It is not difficult to calculate that in this case, given the same kinetic isotope effect of dissociation, the CH_3 group cleaved from the low-temperature compound will be noticeably enriched in the light carbon isotope (if we take as this compound, for example, hexane -- -- by 1.28 percent), while the CH_3 group cleaved from the high-temperature compound will be much less enriched (by only 0.02 percent for hexane). /103

In this example it is not difficult to see the essentials of the method that can be taken as the basis for a study of the geochemical history of compounds relying on their intramolecular isotope effects.

Fundamentally important is the fact that the process parameters can be established by the study of a single compound, while in the case of monoatomic-exchangeable compounds or compounds containing only equivalent atoms, to arrive at α necessitates this system, that is, at least two compounds. With rare exceptions the system components become separated during geologic time, and in isotope geochemistry in practice we have to deal with a single component and several assumptions made with regard to the other. For example, the method of paleothermometry is based on the temperature dependence of δO^{18} in the $CaCO_3$ - H_2O system; here the isotopic composition of carbon in the ancient ocean is hypothetically assumed to be identical to the modern ocean. In this sense a method based on studying intramolecular isotope effects opens up new prospects, since the carrier of information on the process here is not a system in which the test compound was present, but the compound itself.

By investigating intramolecular thermodynamic isotope effects of organic compounds, one can estimate the temperature at which they were formed by using the temperature dependence of the coefficient of isotopic nonuniformity.

For this purpose we must measure the isotopic compositions of the decomposition products of the initial compound, which gives

values of Δ_n; the product of these values for all measured species is written in accordance with Eqs. (II.28) and (II.43) thusly:

$$(\alpha_{i_1}\alpha_{k_1})(\alpha_{i_2}\alpha_{k_2})\ldots(\alpha_{i_n}\alpha_{k_n}) = \frac{\beta_1\beta_2\ldots\beta_n}{\left(\frac{1}{n}\sum_i^n \beta_i\right)^n}\alpha_{k_1}\alpha_{k_2}\ldots\alpha_{k_n}. \qquad \text{(II.44)}$$

By taking the root of degree n from both sides of Eq. (II.44), we get:

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$$\left(\prod_i^n \Delta_n\right)^{\frac{1}{n}} = \frac{\left(\prod_i^n \beta_i\right)^{\frac{1}{n}}}{\frac{1}{n}\sum_i^n \beta_i}\left(\prod_i^n \alpha_{k_n}\right)^{\frac{1}{n}}. \qquad \text{(II.45)}$$

The fraction in the right-hand side of Eq. (II.45) is the coefficient of isotopic nonuniformity ξ (II.33-II.35), whose temperature dependence can be established by theoretical means for different compounds (see Table 32):

$$\left(\prod_i^n \Delta_n\right)^{\frac{1}{n}} = \xi(T)\left(\prod_i^n \alpha_{k_n}\right)^{\frac{1}{n}}. \qquad \text{(II.46)}$$

Thus, by comparing the measured quantity $\left(\prod_i^n \Delta_n\right)^{\frac{1}{n}}$ with the corresponding ξ, we can establish the temperature conditions in which isotopic nonuniformity arose. The quantity $\left(\prod_i^n \alpha_{k_n}\right)^{\frac{1}{n}}$, appearing in (II.46), describing the kinetic isotope effects of the given reaction, can be determined by using the isotopically uniform reference standard compounds and subjecting them to the same method of degradation as the test compound. This method can be employed to study the nature of complex organic compounds found in igneous rocks. This is all the more important in that endogenic bitumens do not differ in the isotopic composition of total carbon from bitumens and crude oils in sedimentary rocks.

Lately numerous reports have appeared on the discovery in igneous rocks and meteorites of organic structures that are

typomorphic for compounds of biological origin. For example K. Kvenvolden and E. Roedder /183/, in studying the composition of inclusions in quartz crystals of high-temperature hydrothermal veins, identified the isoprenoids phytane, pristane, 2,6,10-trimethylpentadecane, 2,6,10-trimethyltetradecane, and so on. The isoprenoid structure characteristic of the phytol segments of chlorophylls until recently were assumed to be a full-fledged indicator of the biological origin of an organic compound. However, H. Studer et al. /225/ was able to isolate isoprenoid hydrocarbons in a process similar to the Fischer-Tropsch process and to separate isoprenoid compounds from carbonaceous matter in carbonaceous chondrites. The use of a method based on a study of the intramolecular distribution of isotopes evidently is capable of resolving the alternative: are given organic compounds of biological origin or the product of abiogenic synthesis. Similarly, analysis of intramolecular isotope effects of organic compounds found in meteorites -- -- carbonaceous chondrites -- can shed light on the temperature conditions in which they were formed. Here this is possibly the only method.

CHAPTER THREE /105

ORGANIC GEOCHEMISTRY OF CARBON ISOTOPES

Fractionation of Carbon Isotopes in Biosynthesis Processes

Isotope Effect of Photosynthesis

A. Near and E. Gulbransen were the first to experimentally establish that the isotopic composition of carbon of organic and inorganic origin differs, and the organic matter is enriched in the lighter isotope. Following them, B. Murphy and A. Near, on measuring the relative content of the C^{12} isotope in the carbon of living organisms, fossil wood, peat, and coal, found that it was approximately 2-3 percent higher than in the carbon of atmospheric carbon dioxide and carbonates. More detailed and exact measurements were then made by H. Craig [68, 138], and later -- by a number of other investigators [117, 194, 195, 206, 227, 233].

It was assumed that the isotope effect of photosynthesis is kinetic in nature. The reactions of photosynthesis are preceded by the physical incorporation of CO_2 in the plant tissue by the dissolving of air carbon dioxide in the plant cytoplasm. Since this process is a nonequilibrium process, it can be accompanied by the kinetic isotope effect. Initially, this hypothesis was made by P. Baertschi [117], based on the analogy between the absorption of CO_2 by plants and its fixation by inorganic absorbers. For example, when carbon dioxide is fixed by a solution of barium hydroxide, some of the carbon dioxide is absorbed by the $Ba(OH)_2$ and deposited as barium carbonate is enriched approximately by /106
1.1 percent in the light carbon isotope compared with the CO_2. R. Park and S. Epstein [206] suggested that differentiation of isotopes during photosynthesis occurs in two stages. At the first stage preferential absorption from atmospheric air of $C^{12}O^2$ and its dissolution in the plant cytoplasm takes place. The separation here is caused by the kinetic effect. The second stage is associated with the synthesis of 3-phosphoroglyceric acid, which is the first more or less stable product of the photosynthetic fixation of carbon dioxide.

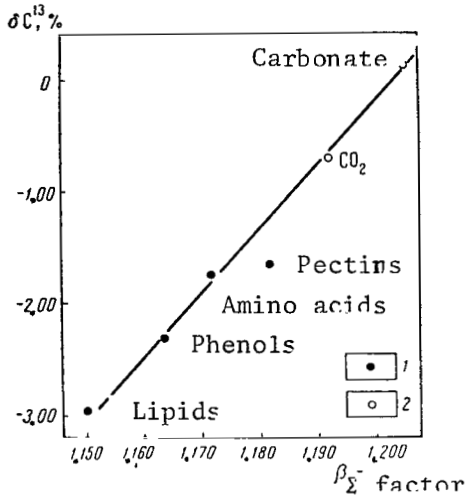

Fig. 22. Comparison of measured values of isotopic composition of constituents of organic matter (1) and the initial inorganic carbon for biosynthesis (2) with the theoretical values of of the factors of these compounds

From the concepts set forth in the preceding sections, the explanation of the mechanisms of biological fractionation can be approached in a different way.

As has been shown, the distribution of carbon isotopes within molecules and between individual biochemical fractions is intimately associated with the values of the thermodynamic isotopic factors of the corresponding compounds, which corresponds to the equilibrium state of isotopic change in biological systems. It is logical to expand the concept of biological isotope equilibrium, by transferring it to the metabolic processes of the organism with its environment. This means that included in their equilibrium system are not only the intrinsically biochemical fractions, but also the initial inorganic compounds and the products of vital activity. In Fig. 22, in addition to the biochemical components of plankton, represented in the same coordinates (isotopic composition and beta-factor) are data characterizing carbon dioxide and carbonate-bicarbonate carbon, which serves as the starting material for the photosynthesizing organisms. They are all related by a common graph, that is, the distribution of the isotopes is such as if the biochemical fractions and the initially organic compounds were components of the single equilibrium isotope-exchange system.

Hence follows the conclusion that the isotope effect of photosynthesis is isotope-exchange in nature, that is, underlying it is the thermodynamic isotope effect. Essentially, the biological fractionation of isotopes consists in rapid isotope exchange being provided for in biological systems. Possibly, this exchange is a variety of the conjugate isotope exchange through a common donor, which can be the enzymes. /107

Isotope Effect of Bacterial Biosynthesis

Phototrophic bacteria performing biosynthesis use as the reducing agent not water, but various reduced forms of sulfur. I. Kaplan et al. [176] indicated the existence of the fractionation of carbon isotopes in this process. More detailed studies were carried out by us together with G. I. Gogotova and M. V. Ivanov [50].

The experiments were carried out with a culture of phototrophic sulfur bacteria Ectothiorodospira shaposhnikovii. The nutrient was a biocarbonate-sulfate mixture (Larsen mixture), where the only carbon source in the nutrient medium was sodium bicarbonate. The biosynthesis was carried out in the light ($30 \cdot 10^3$ erg·cm^2·sec) in anaerobic conditions at 30°C, in 1.5 liter^3 glass vessels.

TABLE 33

RESULTS OF EXPERIMENTS WITH MICROBIOLOGICAL FRACTIONATION OF CARBON ISOTOPES

Date of experiment	Isotopic composition of carbon, percent		C^{13}, ΔC^{13}
	$NaHCO_3$	Biomass	
	Slow development		
1	−1.85*	—	
5	−1.70	−2.86	1.16
6	−1.68	−2.85	1.17
7	−1.59	−2.70	1.11
8	−1.50	−2.59	1.09
	Rapid development		
3	—	−2.66	—
5	−1.30	−2.70	1.40
6	—	−2.76	—
8	−1.19	−2.68	1.49

*Initial biocarbonate

Two series of experiments were carried out: with a fast-growing culture and with a slow-growing culture. The biomass was extracted by centrifuging. The bicarbonate carbon was transferred in the form of CO_2 during titration. The carbon dioxide was /108

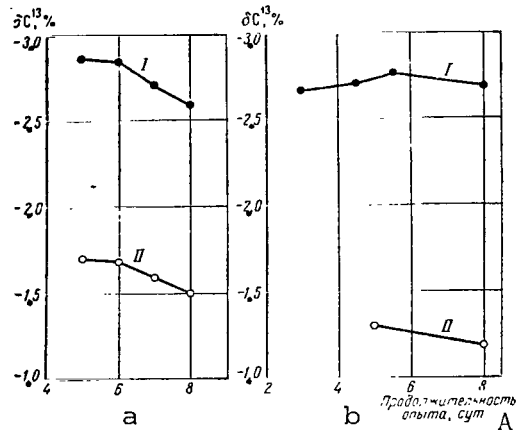

Fig. 23. Isotope effect of the biosynthesis of phototrophic bacteria Ectothiorodospira shaposhnikovii
a. slow-developing culture
b. fast-developing culture
I. change in isotope composition of biomass carbon during experiments
II. change in isotope composition of carbonate substrate during experiment
Key: A. Duration of experiment, days

trapped with bubblers containing barium hydroxide and was deposited as barium carbonate. The isotopic composition of the carbon of the latter and the isotopic composition of the biomass carbon were analyzed in a mass spectrometer. As can be seen from Table 33 and Fig. 23, a considerable isotope effect was observed.

The biomass carbon in all cases was enriched in the C^{12} isotope. The difference in the isotopic composition of carbon between the initial carbonate and the biomass was $\Delta C^{13} = \delta C^{13}_{(carb)} - \delta C^{13}_{(biomass)} = 1.1 - 1.5$ percent. During the experiment, the carbon of the initial bicarbonate was gradually enriched in the C^{13} isotope, which is an obvious consequence of the assimilation by the bacteria of predominantly the isotopically light bicarbonate. The biomass carbon also became somewhat heavier with time, which was due primarily to the increasing weight of the carbon of the initial bicarbonate. At the same time, the fractionation ratio, that is, the difference in the isotopic composition of the carbon of the initial biocarbonate and of the mass of each series of experiments, remained virtually constant.

Thus, during the biosynthesis of autotrophic microorganisms, an isotope effect is observed, consisting in the enrichment of the biomass with the light carbon isotope compared with the bicarbonate substrate. The isotope effect of bacterial biosynthesis in magnitude and sign is close to the isotope effect of the photosynthesis of plants developing on a biocarbonate substrate. In the latter case the isotopic shift is 1.4-2.0 percent.

Noteworthy is the larger fractionation of ratio of isotopes in the case of the fast-growing culture: $\delta C^{13}_{av} = 1.45$ percent as against $\delta C^{13}_{av} = 1.13$ percent for the slow-developing culture. The fractionation ratio changes somewhat with time. If the culture developed slowly, the decrease in the fractionation ratios by the end of the experiment (by the 8th day) was 0.07 percent. The calculated coefficient of biochemical equilibrium κ for the

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slowing-developing culture was 0.33, and for the fast-developing culture $\kappa = 0.47$. In other words, the metabolism carried out by the more inhibited culture ensures a lower degree of the attainment of biological isotopic equilibrium.

The analogy in the nature of the isotope effects during the photosynthesis of plants and in bacterial biosynthesis in our view is due to the fact that in both types of biosynthesis, isotopc fractionation is determined by the frame of reference of isotope-exchange equilibrium.

Heterotrophic Development

If biogenic isotopic effects are thermodynamic in nature and are caused by the biochemical isotopic equilibrium, fractionation must occur only at the molecular level -- of the stage of primary biosynthesis. It must be anticipated then that heterotrophes, that is, organisms developing through the assimilation of finished products of biosynthesis, must not yield isotopic effects.

Actually, numerous measurements showed that zooplankton have the same isotopic composition as the phytoplankton serving it as food [138, 195, 211, 227]. The relative content of carbon isotopes in the soft tissues of marine invertebrates is in the same limits as for marine plants. Animal fats and proteins have an isotopic carbon composition that is analogous to the isotopic composition of the corresponding biochemical constituents of plants [208, 211].

P. Abelson and T. C. Hoering [115] used the property of Chlorella to heterotrophically assimilate carbon in order to estimate fractionation in the nonphotosynthetic assimilation of carbon. They placed a Chlorella culture in a nutrient -- glucose, completely depriving it of illumination and carbon dioxide. The experimental results are partially given in Table 34.

TABLE 34

CONTENT OF C^{13} IN AMINO ACIDS OF HETEROTROPHICALLY DEVELOPING CHLORELLA (GLUCOSE CARBON HAS $\delta C^{13} = 0.0$ %)

Amino Acids	δC^{13}, %	
	Total carbon	Carboxyl group
Aspargic	−0.29	−0.26
Glutamic	−0.03	+0.19
Alanine	+0.05	−0.17

From Table 34 it is clear that practically speaking, no enrichment in the C^{12} isotope occurs for the amino acid of Chlorella grown in the dark. In this case there is also no characteristic difference between the isotopic composition of the carbon of the carboxyl group and the rest of the amino acid molecule. /110

Thus, heterotrophic fixation of carbon and heterotropic development do not lead to a marked fractionation of carbon isotopes.

Environmental Factors Controlling the Isotopic Composition of Organisms

The mechanism of the biological fractionation of isotopes presupposes a significant role of the environment in forming the isotopic composition of organic matter.

The effect of the environment is due to two factors:

1) isotopic composition of the initial carbon, which determines the isotopic composition of the organic carbon formed from it in biogenic equilibrium; and

2) conditions regulating the degree of attainment of biogenic equilibrium.

Air CO_2 is the carbon source for land plants. Its isotopic composition averages -0.7 percent.

Most characteristic for the atmosphere as a whole is the isotopic composition of carbon dioxide in the air of the open ocean, free of the effect of random CO_2 sources. In the air over the Pacific Ocean, δC^{13} is -0.67 to -0.73 percent, averaging -0.71 percent (C. Kiealing, 1961). Carbon dioxide formed through the decaying of organic matter enriches air carbon dioxide in the light isotope. For example, in forest air δC^{13} = -1.10 percent has been established [25].

There is a relationship between isotopic composition and the concentration of carbon dioxide. The amplitude of the diurnal fluctuations in δC^{13} is 0.2 percent. Air carbon dioxide is required to a maximum extent during the daytime and is liberated in the night. Owing to biological fractionation of carbon isotopes, plants preferentially fixate $C^{12}O_2$, which is reflected in the corresponding rise of the concentration of $C^{13}O_2$ in daytime air.

Atmospheric CO_2 forms an exchange system with the bicarbonate of marine water. The fractionation ratio of carbon isotopes in the system CO_2-HCO_3^- established experimentally is 1.0072 [143, 131]

at 25°C, that is, bicarbonate carbon is approximately 0.7 percent enriched in the heavy isotope relative to the carbon of gaseous carbon dioxide.

According to the data of H. Craig et al. [138], of marine water bicarbonate has an average $\delta C^{13} = -0.2$ percent with limits of variation from -0.13 to -0.29 percent. A somewhat heavier carbon of the bicarbonate in marine water with δC^{13} in the range +0.2 to -0.1 percent has been determined in several examples by W. Sackett and W. Moore. Thus, the carbon of marine water bicarbonate is on the average 0.5 to 0.7 percent isotopically heavier than the carbon of atmospheric CO_2. /111

In the coastal waters, bicarbonate is somewhat enriched in the light isotope owing to the incursion from the land of a considerable amount of organic material. In the mouths of rivers, estuaries, and bays, the δC^{13} of bicarbonate fluctuates from -0.5 to -1.1 percent.

Owing to the difference in the isotopic composition of the initial carbon, the isotopic composition of organisms consuming carbon dioxide during photosynthesis and organisms using bicarbonate differs. Land plants are on the average 0.7-1.0 percent enriched in the C^{12} isotope compared to algae. R. Park and S. Epstein [206] arranged an experiment by growing a plant of the same species in water and in air, where the system was supplied with carbon dioxide from the same source. The value of δC^{13} for leaves grown in water was -2.17 percent, while it was -2.7 percent for leaves grown in air.

Of the land plants, the most enriched in the light isotope are the tropical species ($\delta C^{13}_{av} = -2.83$ percent), and the least enriched are the plants of deserts ($\delta C^{13}_{av} = -1.65$ percent). Plants of the temperate zone are characterized by $\delta C^{13}_{av} = -2.51$ percent. Thus, the difference between the mean values of δC^{13}, intrinsic to ecological groups of land plants that are extreme in isotopic composition, is nearly 1.2 percent, where the extremal values of δC^{13} for land plants over all are -1.24 and -3.22 percent.

In the conditions of tropical forests where metabolic activity is at a maximum, plants are more enriched in the light isotopes; in the deserts, in contrast, metabolism is at an extremely low level, to which corresponds weak enrichment of the plants in the light isotope. Plants of the desert, with scanty resources for biosynthesis, permit themselves to be fastidious with respect to the isotopic composition of the carbon they consume. Hence their isotopic composition approaches the isotopic composition of atmospheric CO_2. From the above assumptions, biosynthesis occurring in unfavorable conditions with hindered metabolism, must be characterized by a low coefficient of biochemical equilibrium κ,

and this means also by a smaller isotopic shift between the initial carbon and the carbon of the organic matter. This has been noted also for microbiological biosynthesis.

In view of the relatively low rate of diffusion of CO_2 in water, algae react acutely to local changes in its concentration, just as the content of carbon dioxide in water is intimately associated with the intensity of photosynthetic activity. J. Weber and P. Woodhead [231], on analyzing the change in the δC^{13} of total inorganic carbon of water in the region in which several coral reefs developed, established that carbon sample at night is 0.06-0.15 percent enriched in the light isotope compared to carbon sample in the day -- during the period of maximum photosynthetic /112 activity, that is, here the same pattern as with air carbon dioxide is observed.

W. Sackett, W. Eckelmann, M. Bender, and A. Be [227] found that the isotopic composition of marine plankton from different geographic latitudes differs, which evidently is associated with the temperature of marine water. The mean value of δC^{13} of plankton samples taken from water at a temperature of about 25°C is -2.17 percent, while plankton from high-latitude regions of the South Atlantic with a water temperature about 0°C average δC^{13} = -2.79 percent.

E. Degens, R. Guillard, W. Sackett, and J. Hellebust [194], in order to find out the effect of habitat conditions on the isotopic composition of plankton, conducted laboratory experiments by raising diatom algae of the species Cyclotella nana and Skeletonema costatum under different temperatures of the medium and different carbon dioxide concentrations in the nutrient solution. As a result of the experiments, it was found that the maximum enrichment of the algae in the C^{12} isotope (by 1.8-1.9 percent compared with solution bicarbonate) was observed at high excess concentrations of carbon dioxide, where the δC^{13} of the plankton carbon did not disclose a temperature dependence. When there was a deficiency of CO_2, the nutrient of the plankton in the C^{12} isotope decreases sharply and was 0.9-0.6 percent, compared with the bicarbonate. In this case the δC^{13} of the plankton dependent on the rate of aeration and notably -- on the temperature of the medium. With increase in the temperature, the plankton carbon became depleted in the light isotope. Since the solubility of CO_2 in marine water at 0°C is nearly 2.5 times higher than at 30°C, E. Degens et al. concluded that the temperature dependence is an indirect manifestation of the dependence of the δC^{13} of plankton on the CO_2 concentration. It is precisely in this spirit that they explained the above-presented data of W. Sackett et al. [227].

The growth rate of the culture was also reflected in the isotopic composition of the carbon of its cells. Fast-growing algae utilized more carbon, therefore its isotopic composition

approximates the isotopic composition of the initial carbon [144]. Hence the broad range of δC^{13} values of marine organisms due to the different combination of temperature conditions, CO_2 concentration in the marine water, and the growth rates of organisms can be ultimately associated to some extent with the degree to which biochemical isotopic equilibrium is attained, and also with the dependence of the intramolecular isotopic nonuniformity on temperature.

The dependence between the CO_2 concentration and the isotopic composition of marine plants established by the above investigators is analogous to the above-noted dependence of the isotopic composition of carbon of land plants on the abundance of air carbon dioxide (high content of C^{12} in tropical plants and low -- in desert plants) and on the conditions favoring exchange.

Biogenic Isotope Effects in Carbonates /113

Most carbonate material in Recent sediments is calcite and aragonite shells of marine invertebrates that have settled on the bottom after the death of the organisms. In addition to the clearly organogenic calcite in the more pelagic regions of the ocean, within the limits of the continental slope, and partially of the shelf, fine-grained pelitomorphic calcite is being deposited. According to N. M. Strakhov, fine-grained calcite for the most part is biogenic and is formed through the varying intensive mechanical and, possibly, chemical reworking of organogenic carbonate detritus.

It is assumed that the relative significance of chemical and biological deposition of carbonates has changed during geologic time. Whereas in the Precambrian it was predominantly chemical, with the development of bentonite mollusks at the beginning of the Paleozoic, the inorganic process gradually gave way to the organic, and with the appearance in the Cretaceous of pelagic foraminifera, organogenic calcareous oozes became predominant.

Thus, the great majority of sediments were formed either through the direct accumulation of organogenic calcareous depositions, or else through the chemical redeposition of this material. Sedimentary limestones as a whole are enriched in the heavy carbon isotope. The data in Fig. 24 characterize variations in δC^{13} /114 within the limits of several lithofacial type. The range in the fluctuations of δC^{13} for marine limestones is +0.6 to -0.9 percent. However, 70-80 percent of all carbonates have δC^{13} in the limits +0.2 to -0.2 percent, with a mean that is close to zero.

Enrichment of carbonates in the heavy isotope is considered usually as resulting from the isotopic exchange of carbon in the system CO_2 (atmosphere) -- HCO_3^- (hydrosphere), -- $CO_3^=$ (carbonates).

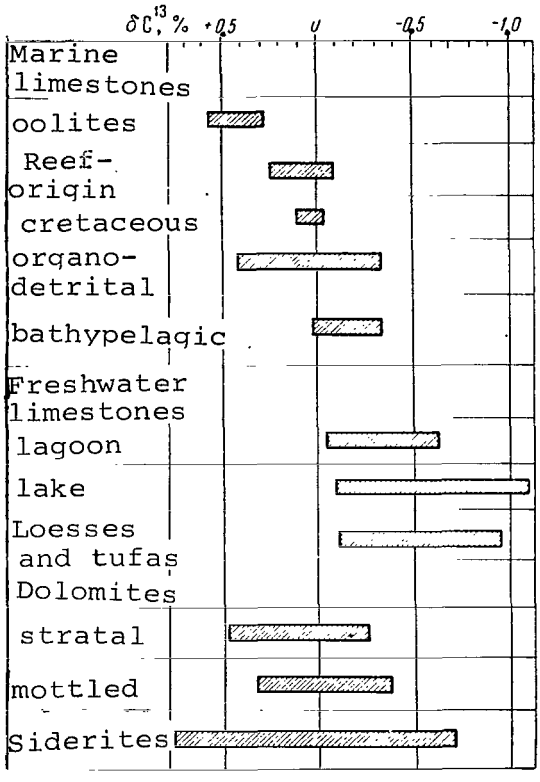

Fig. 24. Isotopic composition of carbon of sedimentary carbonates

In the system, in accordance with the partition coefficient characterizing it, the carbonate must be 1.2 percent enriched in the C^{13} isotope.

Ultimately, the isotopic composition of carbonates must depend on the degree of attainment of equilibrium in the system and on the isotopic composition of the initial carbon dioxide. However, in accordance with the principles of intramolecular biogenic separation of isotopes that we have set forth, this problem can be approached more broadly. If we view the calcite of shells as the metabolic product of invertebrates, then obviously its isotopic composition must occupy its place in the regular series of biochemical fractions in accordance with the value of its β-factor. From Figs. 22 and 25 it is clear that it is actually the case, that is, the organisms form calcium carbonate in an equilibrium fashion, just as any other biogenic fraction. In this case, in the isotopic composition of shell carbonate there must be observed "vital" effects, that is, a relationship between the isotopic composition and species characters and features of the vital activity of the organisms.

Results of analyzing the isotopic composition of shells showed that this relationship actually does exist. H. Gross [161], for instance, observed a stable difference in the isotopic composition of two species of echinoderms: Echinoidea spines is characterized by δC^{13} in the range +0.09 to +0.14 percent, while Echinoidea tests has δC^{13} -0.22 to -0.79 percent. According to data of C. Ross and S. Oana [213] the shells of Osteroidea of Pennsylvanian age are enriched in the light carbon isotope to δC^{13} = -0.59 percent, and Zoantaria from the same deposits have δC^{13} = -0.14 percent.

Pelagic foraminifera has a very even isotopic composition, characterized in various bodies of water by δC^{13} from +0.2 to +0.19 percent [68], from +0.02 to +0.36 percent [161], from +0.12 to +0.19 percent [213]. Markedly enriched in the heavy isotope are the brachiopods. The mean δC^{13} for the Permian brachiopods investigated by W. Compston [136] was +0.43 percent. The δC^{13} we measured for brachiopods of the Podol'sko-Myachkovskiy horizon (Carboniferous) in Orenburgskaya Oblast is +0.57 percent. H. Craig [68] showed that the isotopic composition of the carbon of calcium carbonate deposited by several marine algae, for example, Halimeda, is characterized by positive δC^{13} values, as high as 0.43 percent. The calcite of this origin participated in the formation of the Cretaceous, which accounts for the mean somewhat heavier isotopic composition of Cretaceous limestones.

M.Keith, J. Weber et al. also investigated the variation of the isotopic composition in successive layers of shells. It was found that the inner section of a shell is somewhat enriched in the C^{13} isotope compared with the outer. It was also found that larger individuals of the same species are more enriched in the C^{12} isotope, where the difference is so appreciable (for the species of pelecypod investigated it was 0.6 percent), that any interspecies differences are exceeded. Moreover, it was noted that the younger individuals are enriched in the C^{13} isotope compared with the older representatives of the same species. /115

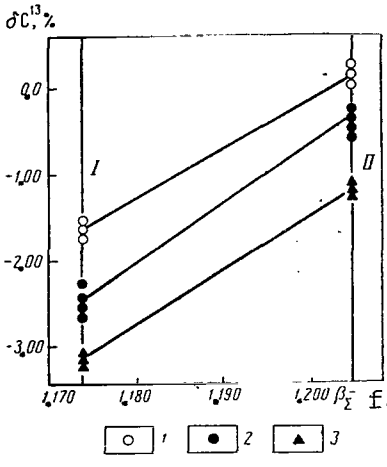

Fig. 25. Comparison of isotopic composition of carbon in soft tissues (I) and shells of invertebrates (II) with thermodynamic isotopic factors characterizing the mean β_{Σ}-factor of organic matter and the β_{Σ}-factor of the carbonate ion
1, 2, 3 -- marine, lake, and river organisms

In Fig. 25 , data on the isotopic composition of carbon in soft tissues and shells of invertebrates from different environments are brought into correspondence with the values of the thermodynamic isotopic factors characterizing the organic material and the carbonates. Use was made of the results of an isotopic analysis of N. Keith et al. [179]. Organic carbon of marine organisms is characterized by δC^{13} from -1.64 to -1.7 percent, and the carbonate of their shells -- +0.02 to +0.11 percent. Organisms living in lakes are enriched in C^{12} (δC^{13} ranges from -2.26 to -2.54 percent); also enriched in the light isotope is carbonate carbon (δC^{13} is -0.24 to -0.49 percent). The synchronous enrichment of the carbon of organic matter and calcium

carbonate of shells is also observed in river organisms. The values of the isotopic shifts are similar, in spite of the species differences of the organism and the essentially different environment of their habitat. The slope of the lines characterizing the degree of biochemical isotopic equilibrium in all cases is approximately the same. The coefficient of biochemical equilibrium κ determined from Fig. 25 is 0.6, that is, of the same order as established in the preceding chapter based on a comparison of the isotopic composition and β-factors of the biochemical fractions.

Thus, isotopic data together with thermodynamic isotopic analysis afford grounds for assuming that the shell carbonate is one of the components of the biological systems of organisms. /116

Carbonate forms of carbon produced by heterotrophes, for example, eggshells, possibly are not included in biogenic equilibria, if one draws analogies with the above-examined distribution of isotopes in heterotrophic development. The measurements of the isotopic composition of eggshells of reptiles and birds, made by R. Folinsbee, P. Fritz, H. Krouse, and A. Roblee [130] show that carbonate carbon is heavier than the carbon in organic tissues and overall is characterized by the δC^{13} limits -0.5 to -1.6 percent characteristic of freshwater carbonates.

Environmental Factors Controlling Isotopic Composition of Carbonates

Just like the isotopic composition of organic-matter carbon, the isotopic composition of the carbon in carbonates depends essentially on external factors. The role of all this involves the nature of the initial carbon.

As was shown, the carbon in the carbonate of the shells of river and lake organisms is isotopically lighter than the carbon of the shells of organisms inhabiting the open seas. River tuff, loess, alluvial limestones, limestone oozes in lakes, and other carbonate sediments associated with freshwater aquatoria are enriched in the light carbon isotope compared with marine limestones, by 0.2-1.2 percent. This is due to the considerable influx of isotopically lighter organogenic carbon dioxide, which is brought in by groundwater to the intracontinental basins. The amount of carbon dioxide arriving from the land is commensurable with the level of the exchange carbon dioxide reservoir of freshwater aquatoria, as the result of which the bicarbonate of freshwater is enriched in C^{12} by an average up to -0.85 percent, that is, nearly 0.6 percent compared with marine bicarbonates.

Results of analyses showed that the higher the relative amount of carbon dioxide arriving from the land, the more enriched

are the limestones enriched in the light isotope. In small freshwater aquatoria (rivers, ponds, and streams), carbonate sediments differ by a high content of C^{12}. In large lakes, the isotopic composition of limestones approximates the isotopic composition of marine limestones.

In terms of conditions of sedimentation, freshwater limestones are akin to littoral sediments of bordering seas, bays, marine lagoons, and so on. In the carbon balance of these aquatoria, a prominent place is occupied by organic carbon arriving from the land, therefore the isotopic composition of littoral carbonate sediments is close to that of freshwater limestones.

Since carbon from the land is brought in by freshwater, ordinarily a relationship is observed between the amount of transported carbon and the salinity of the marine water in a zone abutting the source of the ablation, and as a consequence, a relationship between the salinity of the water and the isotopic composition of the limestone carbon. Enrichment of the limestone in /117
the light isotope corresponds to a decrease in salinity.

W. Mook and J. Fogel [196] observed a successive variation in the isotopic composition of the shells of the same species along the estuary of the Schelde River (The Netherlands) where it flows into the North Sea. Over about 20 km, the salinity of the water as the result of the mixing of fresh and ocean water varied from 0 to 1.8 percent, and the isotopic composition of shells -- on the average, from +0.1 to -1.2 percent. Of course, this relationship, as well as the relationship between the isotopic composition of carbonate carbon and the oxidation-reduction environment is interacting nature. The oxidation-reduction conditions of ocean water are associated with its content of dissolved carbon. The amount of carbon entering the water is determined by the intensity of its gas exchange with the atmosphere, that is, it depends on the same factors as the rate of isotopic exchange of carbon.

The low rate of carbon exchange in reducing conditions not only leads to a disruption of the isotope-exchange mechanism in the systems CO_2-HCO_3^--$CO_3^{=}$ and thus prevents the concentration of C^{13} in limestones, but also promotes an establishment of a short-circuited exchange cycle between carbonate carbon and the isotopically lighter organogenic carbon dioxide. Always present in ocean water is a considerable amount of organogenic carbon dioxide liberated during respiration by marine organisms and the decomposition of organogenic detritus (δC^{13} = -2.0 percent). In stagnant, poorly aerated water it forms local fields with a predominant content of isotopically light CO_2. Assimilations of CO_2 owing to the lower rate of its diffusion are dissipated extremely slowly. The carbonates depositing in this environment are always noticeably enriched in the light isotopes -- usually from -0.2 to -0.10 percent.

The dependence of the isotopic composition of carbonate carbon on the conditions in which carbonates are deposited was used in several studies to reconstruct the oxidation-reduction environment and the salinity of ancient basins. Thus, a study [45] of the isotopic composition of carbon in the Upper Jurassic and Lower Cretaceous carbonates of Western Siberia, with different facial-lithologic and paleoecologic characteristics, afforded the conclusion that the isotopic dates for the most part quite reliably characterize the gas regime of the ancient bodies of water, the degree of aeration of the basin, and identify the conditions favorable for the development of benthic fauna -- a deep zone of the shells, the shallow sea of normal salinity, where δC^{13} has a positive value (averaging +0.08 percent), and basins that are unfavorable in this respect -- containing hydrogen sulfide contamination of the benthic water, bathypelagic lagoons with increased concentration of salts dissolved in water, significantly freshened aquatoria, and so on, with negative δC^{13} values (from -0.31 to -1.10 percent, and in one case -2.02 percent).

Diagenesis and Fossilization of Organic Matter /118

Organic Matter in Sediments

The most important stage along the path of the transformation of organic matter into fossil fuels is its diagenesis in subaqueous sediments, where it is subject to profound degradative changes.

Investigations of the isotopic composition of organic carbon in juvenile sediments showed that organic matter of oozes are enriched overall in the light carbon isotope compared with the initial carbon of marine organisms [36, 172, 180, 214, 217, 220]. The mean isotopic composition C_{org} of marine sediments is -2.14 percent, while the mean isotopic composition of the carbon of marine organisms is -1.6 percent.

Together with V. I. Bagirov, we conducted investigations of the organic sediments of the Caspian Sea (Fig. 26). The benthic deposits were sampled at the latitude of the city of Derbent with a straight-flow ground tube from a sea depth of 310 m (station A) and 775 m (station B). The length of the cores was 3.40 and 5.75 m, respectively. The exposed profile, pertaining to the Neocaspian Stage is represented chiefly by aleurite-clay oozes. The isotopic composition of organic-matter carbon discloses a relationship with the stratigraphic subdivision of the benthic deposits. In both stages investigated, a noticeable depletion of organic matter in C^{12} corresponds to the early stage of the accumulation of Neocaspian sediments. This is evidently associated with the fact that the diagenesis of organic sediments in the early Neocaspian occurred in conditions of a less reducing

environment than in the subsequent period of time. Along the boundary of the lower and upper layers there is a sharp variation in the content of C_{org} in the sediments. Sediments corresponding to the later stage of sedimentation are colored black owing to the abundance of hydrotroillite and have the order of hydrogen sulfide. Deposits of the Early Neocaspian are lighter and contain much less iron sulfides. The trend in the variations of the isotopic composition of C_{org} with depth (within the upper stratigraphic subdivision) at the two stations investigated is dissimilar. At station A (310 m) the variations are not constant, while at the station B (775 m), beginning at a depth 5 cm from the surface of the sediment, there is a gradual enrichment of organic carbon with C^{12}, reaching a maximum value (δC^{13} = -2.53 percent) at the foot of the upper layer of the Neocaspian sediments.

The trend toward a successive accumulation of C^{12} from the more juvenile to the more ancient sediments has also been noted earlier and S. Silverman suggested that this phenomenon is due to the gradual concentration in this sediment of the isotopically light lipid fraction that is more resistant to decomposition. This is valid as a special case. Taking note of the intramolecular distribution of isotopes, we can conclude that the enrichment of the org organic matter in C^{12} during diagenesis is due first to decarboxylation, as the result of which isotopically heavy carbon CO_2 of the carboxyl groups is removed. Then the peptide bonds are broken, the proteins are hydrolyzed, and the sugars are decomposed, on the one hand, and the fats, decarboxylated amino acids, the ligninlike compounds, and compounds with cyclic structures of the terpenoid type are consolidated, on the other hand. All these processes lead to the accumulation in the organic matter of C^{12}, and moreover from /120 the chemical standpoint they are most probable upon the degradation and humification of organic matter.

Organic matter in benthic oozes in the uppermost surface layers is enriched in C^{12} compared with the carbon of the initial organisms. This indicates that a certain fraction of these processes are completed already in the water depth before the deposition of the organic remains on the bottom.

Features of subaerial and subaqueous diagenesis

Carbon dioxide in the diagenesis of organic matter can be formed in two fundamentally different ways:

$$\text{(I)}\quad C_xH_yO_z \rightarrow CO_2 + C_{x-1}H_yO_{z-2};$$

$$\text{(II)}\quad C_xH_yO_z + O_2 \rightarrow CO_2 + C_{x-1}H_yO_z.$$

Intramolecular isotopic nonuniformity is responsible for the substantially different nature of the formation of the isotopic composition of carbon dioxide forming through the decomposition of organic matter (I) and its oxidation (II). Degradative carbon

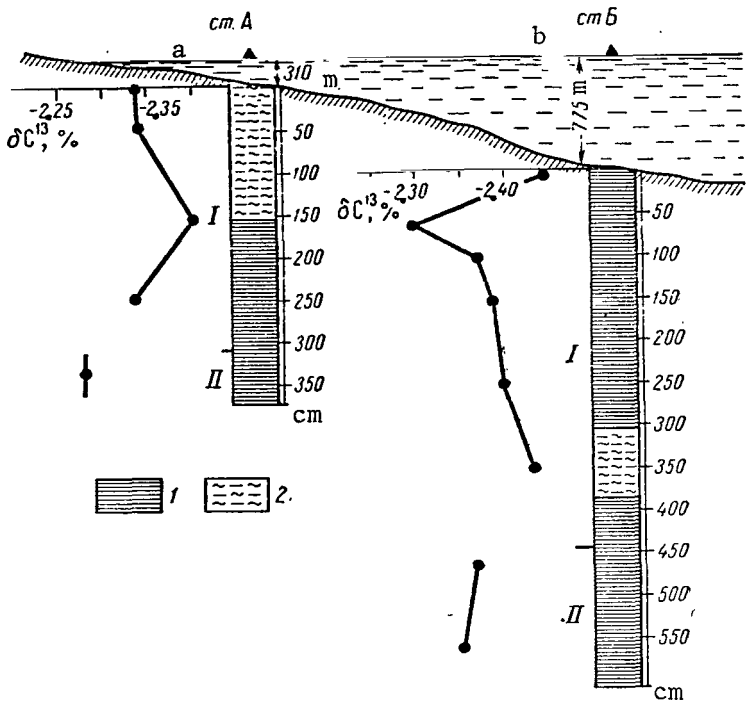

Fig. 26. Change in isotopic composition of organic-matter carbon in the benthic sediments of the Caspian Sea (Neocaspian deposits)
1. clay sediment
2. clay-aleuritic sediment
I, II. late and early stages of sedimentation
Key: a. Station A
b. Station B

dioxide, inheriting the carbon of oxygen-containing functional groups, is enriched in the isotope through concentration in these groups of C^{13}. Carbon dioxide, forming as the oxidation product of organic matter, has an isotopic carbon composition coinciding with the mean isotopic composition of the carbon of oxidizable organic matter. Process I is carried out in anaerobic conditions, and process II -- in aerobic conditions.

Thus far the view has been held that isotopic shifts in the degradation of organic matter are due principally to the kinetic isotope effect, which essentially consists of the predominant breaking of bonds of the C^{12}-C^{12} type compared with C^{12}-C^{13}. Hence any transformation products of the organic matter must be enriched in C^{12}.

At one time, the kinetic isotope effect was studied in detail with the example of various reactions of decarboxylation, especially by J. Bigeleisen et al. (1949-1952). From the data of several investigators, the kinetic isotope effect in the carboxylation of organic acid fluctuates in the limits 1.015 to 1.040, with a mean of 1.030, which corresponds roughly to 3 percent enrichment in C^{12} of the liberated carbon dioxide and the depletion of C^{12} of the residual organic carbon in the initial reaction stage.

These data apparently contradict the assumption that decarboxylation reactions can lead to the enrichment of the residual organic carbon (for example, in the sediment) in the light isotope. But /121 this contradiction actually most graphically reveals the determining role of intramolecular isotope effects. The point is that experiments on the carboxylation was carried out with preparations that have been artificially enriched in C^{13}. Natural intramolecular variations of isotopic composition cannot play any role against this background. As a result, the kinetic isotope effect was measured in the pure form and became manifested in accordance with the anticipations in the enrichment of the cleaved CO_2 with C^{12}.

In natural samples, intramolecular enrichment in C^{13} of the carbon forming C-O bonds proves to be a stronger factor than the kinetic isotope effect operative in cleavage. The actual value of the latter can be established by measuring the isotopic shift between the carbon of the cleaved CO_2 and the initial carbon of the carboxyl group (in not of the entire organic compound as a whole). I. Kaplan and S. Rittenberg [177] established that when lactate is microbiologically oxidized by sulfate-reducing bacteria, the metabolic CO_2 is enriched in the light isotope relative to the carboxyl carbon, by 0.5-1.1 percent. In this case they take place essentially the decarboxylation of the lactate, since the CO_2 liberates from the lactate forms air exclusively owing to the cleavage of the carboxyl group:

$$2CH_3CHOHCOOH + SO_4^{=} \rightarrow 2CH_3COOH + \\ + 2CO_2 + S^{=} + 2H_2O.$$

The observed isotopic shift therefore can be entirely attributed to the kinetic isotope effect. Unfortunately, in this study the isotope shift of the CO_2 was not measured with respect to the total carbon in the lactate. Recently, V. Smejkal, F. Cook, and H. Krouse [220], in investigating the similar process, noted that the CO_2 released upon the oxidation of lactate by microorganisms is enriched in C^{13} compared to total lactate carbon. These investigators did not present data on the isotopic shift of CO_2 relative to the carboxyl carbon, but by comparing the two studies mentioned above, we see that in spite of the presence of the kinetic isotope effect leading to the enrichment in C^{12} of the carbon dioxide carbon compared to the carbon of the initial structural group (carboxyl), the existence of intramolecular isotopic

nonuniformity (in particular, the enrichment of the carboxyl group in C^{13}) leads to the released carbon dioxide ultimately proving to be isotopically heavier than the organic compound. In complex polymeric compounds of the humus type, the significance of kinetic isotopic effects in degradative processes evidently is low. A discussion of this is given in Chapter Six. Evidently, we must reexamine concepts of the role of kinetic isotopic effects in the transformation of organic matter, which thus far has been assigned decisive significance by numerous investigators, including the present author. /122

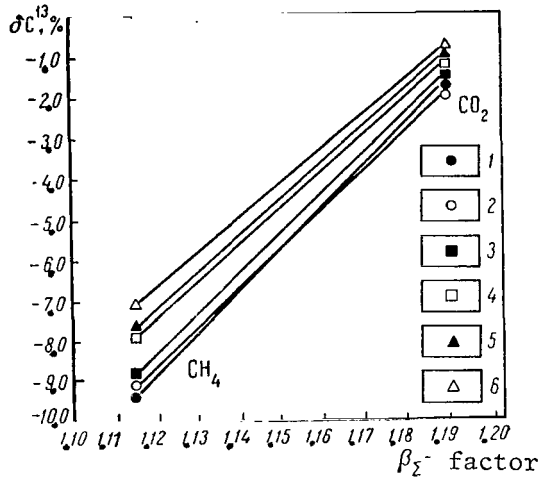

Fig. 27. Comparison of isotopic composition of carbon in the bacterial fermentation products of methane and carbon dioxide with theoretical β_Σ-factors characterizing these compounds. These experimental data taken from a study by N. Nakai [201] and correspond to a different conditions of experimental duration of 3, 7, 11, 15, 20, and 25 days (1-6).

Degradative carbon dioxide is also formed together with methane in methane fermentation. Reaction (I) in this case takes on the following form: $C_xH_yO_z \rightarrow CO_2 + CH_4 + C_{x-2}H_{y-4}O_{z-2}$. The foregoing discussing biogenic isotopic equilibria suggests that carbon dioxide and methane, being in this case the metabolic products of microorganisms, must have different isotopic composition, corresponding to different values of their β-factors. Experimentally, this effect has long since been established. W. Rosenfelb and S. Silverman, as well as N. Nakai [201] in experiments with the fermentation of methane or acetic acid observed the formation of methane anomalously enriched in the light carbon isotope to 0.8 percent at 30°C. In contrast, metabolic carbon dioxide is 0.3-0.7 percent depleted in C^{12} compared to initial carbon. Fig. 27 compares the isotopic compositions of methane and carbon dioxide with their β-factors. This comparison again confirms the existence of a biogenic isotopic equilibrium, where the coefficient of biochemical equilibrium in this process is very high, have the value of κ approaches unity. In natural conditions, the products of methane fermentation are formed in swamps and in moist, organic matter-saturated sediments when there is an oxygen deficiency. It is precisely in these conditions that S. Oana and E. Deevay [203] first found anomalously light methane. The maximum

Variations in the isotopic composition of CO_2 carbon within each soil type, as well as between soils of different types are due principally to the intensity of gas exchange with the atmosphere (especially is soils with low carbon dioxide concentration).

Secondary Materials in the Diagenesis Zone

Depending on in which direction and in which conditions the diagenesis of organic matter takes place, products of extremely dissimilar isotopic composition can be formed (Fig. 29).

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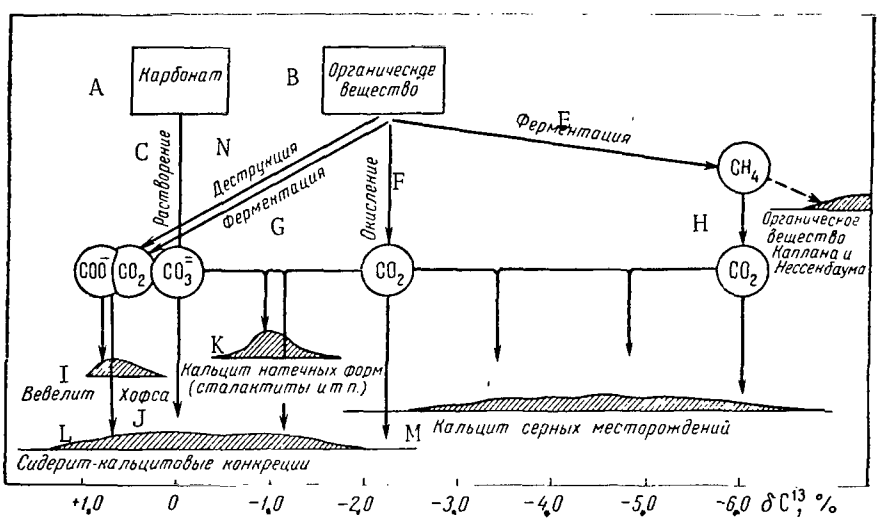

Fig. 29. Scheme for formation of isotopic composition of carbon in secondary minerals in diagenesis zone

Key:
A. Carbonate
B. Organic matter
C. Dissolution
D. Degradation
E. Fermentation
F. Oxidation
G. Fermentation
H. Organic matter, Kaplan and Nessenbaum
I. Whewellite
J. Hoefs
K. Calcite of flowing forms (stalactites and and so on)
L. Siderite-calcite concretions
M. Calcite of sulfur deposits
N. Degradation

enrichment of methane carbon by the light isotope reached a value characterized by $\delta C^{13} = -8.02$ percent, which is more than 5 percent higher than the concentration of C^{12} in the initial plant material. Conversely, carbon dioxide in all cases proved to be depleted in C^{12} by 0.5-1.5 percent compared with the plant carbon and soil CO_2. This pattern of the distribution of carbon isotopes in the constituents of swamp gas was subsequently confirmed [74, 89, 140, 200].

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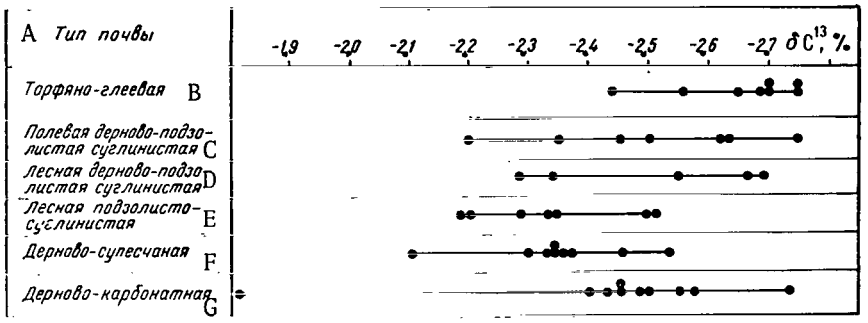


Fig. 28. Isotopic composition of CO_2 carbon and and soils of different types (Moscow Oblast)
Key: A. Soil type
B. Peat-gumbo
C. Field sod-podzolic loamy
D. Forest sod-podzolic loamy
E. Forest podzolic-loamy
F. Sod-sandy loam
G. Sod-carbonate

In contrast to subaqueous sediments and swamps, in soils predominantly oxidative processes are developed, that is, processes of the type (II), as a result of which carbon dioxide is formed of the same isotopic composition as the original oxidized carbon.

Literature data on the isotopic composition of soil CO_2 evidently are limited only to a single study on the isotopic composition of several types of soils developed in Moscow Oblast (Fig. 20) [25].

Extremal values of δC^{13} in the sample studied are -1.8 and -2.8 percent, that is, they correspond to the extreme values of the range of variation in the isotopic composition of carbon characteristic of land plants; the mean composition of carbon in soil CO_2 ($\delta C^{13} = -2.47$ percent) is very close to the isotopic mean composition of the initial plant carbon ($\delta C^{13} = -2.55$ percent).

Carbon dioxide formed in the oxidation of organic matter, on entering into solution, leaches carbonate material. As a result, the biocarbonate ion of dissolved limestone appears in the solution along with the bicarbonate of organic origin:

$$CaC^{13}O_3 + C^{12}O_2 + H_2O \rightleftarrows Ca^{++} + HC^{13}O_3^- + HC^{12}O_3^-.$$

Secondary calcite precipitating from the solution inherits in equal measure the isotopic composition of both limestone as well as organic carbon. Processes of this type are typical for subaerial conditions. At one time we closely investigated the isotopic composition of the carbon in karst formations: stalactites, stalagmites, and other flowing forms from the caverns of the Crimea, Caucasus, Permskaya Oblast, the Moscow Area, and also Yugoslavia, Romania, and Cuba. Characteristic of them are δC^{13} values from -0.5 to -1.5 percent, that is, intermediate between the values characteristic of carbonate carbon and the carbon of soil carbon dioxide [29, 38]. It was shown that from the growth rings of stalactites, one can reconstruct the details of the evolution of the soil-climatic environment [39]. M. Geyh and B. Schillat [155] also conducted this type of investigation.

Mixing of organic and carbonate carbon dioxide occurs obviously also in the formation of carbonate concretions, where the proportions of this mixture can serve as an index of the change in the /125
oxidation-reduction environment in the sediment during the course of diagenesis. In the concretions from the Bayosskiye clays of Dagestan were investigated together with Y. P. Girin, successive variation in isotopic composition from the center to the periphery of concretions was observed: from -2.27 to -0.96 percent [37].

In several cases carbonate concretions are formed in sediments that are nearly entirely depleted of carbonate material. Nonetheless, they proved to be isotopically notably heavier than the only initial organic carbon that is possible for them. Several mineral bodies of similar nature that we investigated with Z. V. Timofeyeva are characterized by δC^{13} values of -0.45 to +1.2 percent, where one sample of siderite concretion had C^{13} = +1.6 percent, in this case, it must be assumed that isotopically heavy degenerative carbon dioxide served as the initial carbon for the formation of the carbonates. The same also can be said about the isotopically heavy carbonates (δC^{13} = +0.54 - +1.9 percent) of diagenic origin observed by K. Murata et al. [199]; they were deposited as infrequent intercalations 0.3-0.9 m thick in the Myocene diatom shales of California.

To account for the cases of C^{13} enrichment of diagenetic carbonates, several investigators have involved the microbiological system CO_2 - CH_4, since it is known that isotopically heavy carbon dioxide forms in the system [168, 199, 213]. It is possible that in some cases it is precisely this mechanism that it is at work,

but this is not necessarily so. Degradative CO_2 is enriched in C^{13} owing to the features of the intramolecular distribution of isotopes, of which we have spoken. Therefore upon the degradation of organic matter, isotopically heavy carbon dioxide can be released into the ooze solution regardless of processes of methane fermentation.

In sediments are found products of the direct mineralization of carboxyl carbon -- salts of carboxylic acids, including oxalates (salts of oxalic acid). The latter are present in the form COO·COO·Ca as a part of the mineral whewellite ($CaC_2O_4nH_2O$). The isotopic composition of this rare mineral has been investigated by J. Hoefs, who obtained δC^{13} for three samples, +0.78, +0.76, and +0.07 percent. J. Hoefs notes: "... if oxalate in whewellite is biogenic, then this is the first case of the discovery of biogenic heavy carbon.... The question of what kind of fractionation led to the formation of this heavy carbon is unanswered.... One possibility lies in the partial bacterial decomposition of oxalate into isotopic whewellite carbon dioxide and the increasing weight of the residual oxalate" [167, p. 396]. This is the traditional explanation from the isotopic-kinetic standpoint. In our view, the whewellite investigated by J. Hoefs can be viewed as the succesful example of an isotopically heavy mineral formed through the direct utilization of degradative carbon dioxide (carboxyl carbon dioxide), whose carbon initially was enriched in the heavy /126 isotope through intramolecular isotopic nonuniformity caused by biogenic equilibria.

Biochemical methane during diagenesis can be involved in a new biological cycle, as a result of which organic compounds can be formed that are altogether unusually enriched in C^{12}. I. Kaplan and A. Nissenbaum [175] in sulfur deposits (Berri, Israel) found inclusions of organic matter whose carbon had δC^{13} values from -8.25 to -8.93 percent. But evidently this is an exceptional case. Much more often isotopically like calcium is encountered. For example, J. Hathaway and E. Degens [166] determined δC^{13} values from -2.80 to -6.06 percent for samples of aragonite and magnesium-containing calcium from sand deposits (continental slope of the east coast of North America). They assumed that the probable carbon source for these carbonates was methane oxidized to CO_2 chemically or microbiologically. In the literature are described numerous cases in which isotopically light calcite was found to be present in sulfur deposits (H. Feeley, and J. Kalb, 1957; H. Todd et al., 1954; H. Dessau, R. Gorfiantini, and E. Tongiorgi, 1959-1969; H. Dessau, M. Jensen, and N. Nakai, 1962; A. P. Vinogradov, V. A. Grinenko, and V. I. Ustinov, 1961, 1964; E. Cheeney and M. Jensen, 1965; E. Cheeney, 1967; G. P. Mamchur, 1968, 1969). The isotopic composition of calcite fluctuates from -1.5 to -7.5 percent. Paragenesis of calcite and native sulfur is caused by the reaction $SO_4^{=} + 2C_{org} \longrightarrow S^{-} + 2CO_2$, during which bacteria reduce the sulfate to elemental sulfur, and by means of the sulfate

oxygen the organic matter is oxidized. However, only on the basis of this reaction it is impossible to explain the enrichment of calcite in the light isotope to a level that is much higher than the concentration of C^{12} in the organic matter. Doubtless, isotopically light methane participates in forming the calcite. For the carbon of methane to be able to be utilized in calcite, it is necessary at some stage to oxidize it. Possible schemes of this process have been discussed by us earlier [29].

Coalification

Coalification occurs in anaerobic conditions, usually when an organic mass is buried beneath the groundwater level. The factors of metamorphosis -- temperature and pressure -- promote the process of coalification and lead to the successive increase in the concentration of carbon from 60-70 to 90-98 percent in the series lignite -- hard coals -- anthracites. Coals with a high degree of metaphism are usually structure-less gelified matter, but for the most part the preserved traces of the initial structure of the plant tissue and contain shaped elements, that is, organic inclusions with the structure of the plant microcomponents (cuticles, spores, and so on).

The isotopic composition of coal as a whole coincides with the isotopic composition of the carbon of land plants. This was /127
demonstrated for the first time by B. Murphy (1941).

Through the examination of the isotopic composition coals, essentially we had the only opportunity of estimating the abundance of isotopes in plants of past geological epochs, since in contrast to other organic fossils, coals lie in the site of their formation and their age corresponds to the geologic age of the country rock.

Investigations showed that during the Phanerozoic the isotopic composition of coals, thus also plants changed little and without visible correlations [68, 136, 139, 218, 233].

As was indicated above, intraspecies fluctions of the isotopic composition of plants belonging to any physical-geographic province embrance nearly the entire range of δC^{13} values characteristic of plants as a whole.

In sedimentary rocks, a coal bed within the limits of the given coal basin will correspond to a specific paleoecological group. Samples taken from the same coal bed (Newcastle Basin, Australia) at an interval of about 20 km yielded δC^{13} values deviating by no more than 0.07 percent from the mean, -2.29 percent, where most of the coal samples within the limits of the experimental error proved to be of identical isotopic composition

[136]. This uniformity of isotopic composition of carbon within the limits of a coal bed testifies to the essential homogenization of the initial organic mass during coalification. Coals with with varying metamorphism on the average are approximately the same in isotopic composition. This was first pointed out by F. Wickman [233]. We noted a trend toward a narrowing of the interval of δC^{13} variations in coals with a high degree of metamorphism, explain the "averaging of the isotopic composition during coalification as resulting from losses of some fractions that were extreme in isotopic composition" [29].

The absence of a correlated change in the isotopic composition of coals with different degrees of metamorphism produced a quandry, since at all stages of coalification methane is given off, which is substantially enriched in the light isotope. It would appear that with increasing the degree of metamorphism the heavy carbon isotope must be accumulated in coals.

An idea of the intramolecular isotopic nonuniformity lets us understand the heart of the matter. If the composition of a coal is represented by the following formula $C_XH_YO_Z$, then on the average for each carbon atom we arrive at the following set of bonds:

$$(4-y-2z)\,L_{C-C}+yL_{C-H}+zL_{C=O};$$

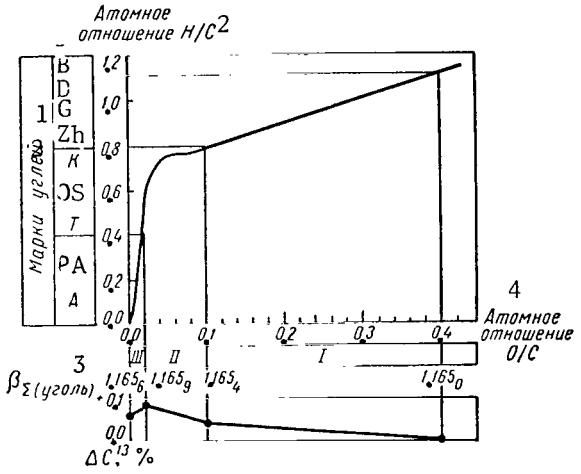


Fig. 30. Scheme of variation in isotopic composition of carbon during coalification (I-III -- stages)

Key: 1. Coal grades
2. Atomic ratio
3. $\beta_{\Sigma(coal)}$
4. Atomic ratio

Hence we have the thermodynamic isotopic factor characterizing organic matter, /128

$$\beta_\Sigma = 1+\left(4-\frac{H}{C}-2\frac{O}{C}\right)L_{C-C}+\frac{H}{C}L_{C-H}+\frac{O}{C}L_{C=O},$$

where H/C and O/C are the atomic ratios of the corresponding elements in coal.

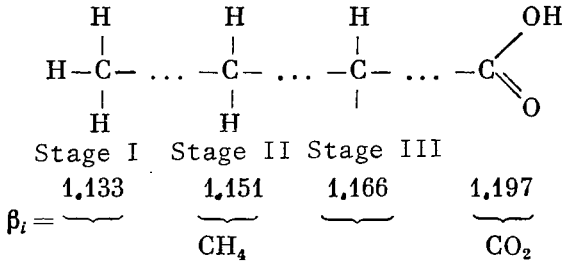
Fig. 30 shows the curve [139] of variation in the atomic ratios of carbon, hydrogen, and oxygen in coal during coalification: predominantly CO_2 is released at the early stages, and beginning with the stage corresponding to coals of grades Zh and K, methane increasingly predominates in the volatiles. Corresponding to the early

lignite stage of coalification is the point on the curve in the graph corresponding to the atomic ratios H/C = 1.11 and O/C = 0.4. When the values of the isotopic bond numbers are used, it is not difficult to establish the thermodynamic isotopic factor for organic matter at this stage -- $\beta_{\Sigma_0} = 1.165$.

The change in isotopic composition of coal during coalification can be traced by calculating the β_Σ-factor for each subsequent stage and by comparing it with the initial value: $\Delta C^{13} = (1 - \beta_{\Sigma_0}/\beta_\Sigma)10^2$. Here we must consider that owing to intramolecular biogenic isotopic equilibrium at different stages of the process the carbon of different isotopic composition will be eliminated.

In the form of CH_4, first the carbon of the CH_3 groups is eliminated, then the carbon that has two C-H bonds, and finally, in strongly carbonized material the carbon having a single C-H bond enters into methane.

This can be represented thusly: /129



In the form of the dioxide, predominantly the carbon that is part of the oxygen-containing functional groups is cleaved.

Overall, the process of separation of volatiles can be expressed by the reaction

$$C_xH_yO_z \rightarrow nCO_2 + mCH_4 + C_{x-n-m}H_{y-4m}O_{z-2n}.$$

Let us examine the change in the β_Σ-factor during coalification, by referring to the graph in Fig. 30. We provisionally single out three stages. We assume that I is the stage embracing the coalification all the way to the formation of grade Zh coals, and that methane is formed from carbon of CH_3 groups characterized by a β_i-factor of 1.133. As we can see from Fig. 30, the elemental composition of coal during this process changes from C:H:O = 1:1.11:0.4 to C:H:O = 1:0.8:0.1.

Hence,

$$CH_{1.11}O_{0.4} \rightarrow 0.166CO_2 + 0.139CH_4 + C_{0.695}H_{0.556}O_{0.069}.$$

It should be noted that if we know the atomic ratios C:H:O for coals whose compositions correspond to the beginning and end of the

particular stage of coalification, then by uncomplicated transformations we can get an expression for the coefficients n_{CO_2} and m_{CH_4} in the coalification equation:

$$n_{CO_2} = \frac{\left(\frac{H}{C}\right)_0\left(\frac{O}{C}\right)_1 - \left(\frac{H}{C}\right)_1\left(\frac{O}{C}\right)_0 + 4\left(\frac{O}{C}\right)_0 - 4\left(\frac{O}{C}\right)_1}{8 - 2\left(\frac{H}{C}\right)_1 - 4\left(\frac{O}{C}\right)_1};$$

$$m_{CH_4} = \frac{\left(\frac{O}{C}\right)_0\left(\frac{H}{O}\right)_1 - \left(\frac{H}{O}\right)_0\left(\frac{O}{C}\right)_1 + 2\left(\frac{H}{O}\right)_0 - 2\left(\frac{H}{C}\right)_1}{8 - 2\left(\frac{H}{C}\right)_1 - 4\left(\frac{O}{C}\right)_1}.$$

Let us determine the thermodynamic isotopic factor by the end of stage I from the relation

$$1.1650 = 0.166 \times 1.197 + 0.139 \times 1.133 + 0.695\beta_{\Sigma_1},$$

whence β_{Σ_1} = 1.1654 and, therefore, the value of the isotopic shift δC^{13} = +0.04 percent. /130

Coal having a given composition is the starting material for the next coalification stage, embracing the stages corresponding to coals of grades K, OS, and T. We assumed that at this stage methane is formed chiefly from the carbon of the CH_2 group characterized by β_i = 1.151. The elemental composition of the coals changes from C:H:O = 1:0.8:0.10 to C:H:O = 1:0.4:0.02.

The coalification equation is

$$CH_{0.8}O_{0.1} \rightarrow 0.042CO_2 + 0.116CH_4 + C_{0.842}H_{0.336}O_{0.017};$$

$$1.1654 = 0.042 \times 1.197 + 0.116 \times 1.151 + 0.842\beta_{\Sigma_2}.$$

Calculation gives β_{Σ_2} = 1.1659 for coal by the end of stage II. The isotopic shift compared with the initial organic material at the early lignite stage is +0.09 percent.

Finally, at the last anthracite stage we have:

$$CH_{0.4}O_{0.02} \rightarrow 0.01CO_2 + 0.100CH_4 + 0.89C;$$

$$1.1659 = 0.01 \times 1.197 + 0.100 \times 1.166 + 0.89\beta_{\Sigma_3},$$

whence β_{Σ_3} = 1.1656 and δC^{13} = +0.06 percent.

Thus, calculation shows that the isotopic composition of coal during coalification changes extremely slightly: variations do not exceed the limits of a tenth of a percent, in spite of the separation of a considerable mass of the volatiles, whose carbon isotopic composition appreciably differs from coal of carbon. The absence of the variation in the isotopic composition of carbon with increase in degree of metamorphism of coal, noted by different investigators, is thus associated with the nonuniformity of the organic matter.

From the last equation it is clear that at the anthracite stage of metamorphism of bituminous coals, the liberation of methane somewhat depleted in C^{12} relative to the initial coal is possible. Instances in which isotopically heavy methane was present in gaseous accumulations have actually been described. For example, the gases of Northwest Germany, genetically associated with bituminous coals, contains methane with δC^{13} from -2.49 to -2.85 percent [222]. U. Colombo, F. Gazzarrini, M. Teichmuller, et al. [128] desorbed from anthracites methane exhibiting δC^{13} from -1.68 to -2.50 percent, while the isotopic composition of anthracite was -2.50 percent. In the Guardakskaya salt-bearing strata of the Amudar'inskaya syneclise, we detected methane characterized by δC^{13} = 2.64 percent (Iolotanskaya Platform, square 1, J_3km +·t). Coal-bearing strata are extensively developed in the underlying deposits here. Correlations of the change in the isotopic composition of gases during coalification are discussed in Chapter Six dealing with gases in sedimentary rocks.

/131

CHAPTER FOUR

PETROLEUM

General Correlations of Variations in the Isotopic Composition of Petroleum Carbon

The first data on the isotopic composition of carbon in petroleum were obtained by S. West, H. Craig, and A. V. Trofimov. But the foundation work obviously must be regarded as the well-known study by S. Silverman and S. Epstein [220]. These investigators made a comparative analysis of the isotopic composition of crude oils of different ages, as well as natural gas and organic matter from Recent and ancient sediments.

Various investigators have conducted isotopic analyses of the carbon in crude oils of the USSR. The δC^{13} values, as can be seen from Fig. 31, do not exceed the limits of 1 percent. This range is even narrower for some regions. Thus, all the investigators of crude oils of the Volga-Ural area (chiefly based on our data for the Permian Ural Area) are characterized by δC^{13} from -2.65 to -3.05 percent, that is, the fluctuations are only 0.4 percent.

J. Hunt and E. Degens in a review study presented at the Symposium on Stable Isotopes in the city of Leipzig (1967), in summing up the results of analyses of the isotopic composition of crude oils made by foreign investigators, chiefly on North American crude oils, noted more or less smooth trend toward enrichment in the light isotope with a rise in the age of country rock. The Perm-Triassic crude oils, relatively enriched in C^{12}, depart from the monotonic dependence.

It bears noting that at one time S. Silverman and S. Epstein [220], based on a relatively small number of determinations, indicated a difference in the isotopic composition of Paleozoic and Tertiary crude oils. Among the Paleozoic crude oils of the Permian Basin of the United States, according to data of K. Kvenvolden and R. Squires [184], a tendency is disclosed to depletion of the more

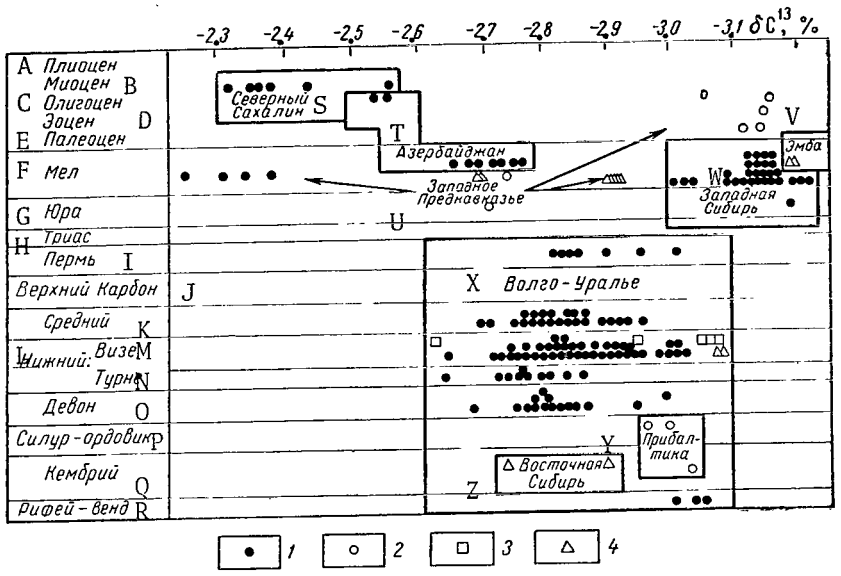


Fig. 31. Isotopic composition of carbon in crude oils from different areas of the USSR based on our data (1), the data of T. A. Botneva, P. Myuller, and I. Maas [4] (2), V. S. Vyshemirskiy, and Ye. F. Doil'nitsina [22] (3), and F. A. Alekseyev et al. (4)

Key:
A. Pliocene
B. Miocene
C. Oligocene
D. Eocene
E. Paleocene
F. Cretaceous
G. Jurassic
H. Triassic
I. Permian
J. Upper Carboniferous
K. Middle
L. Lower
M. Visean
N. Turonian
O. Devonian
P. Silurian-Ordovician
Q. Cambrian
R. Riphean-Wendian
S. Northern Sakhalin
T. Azerbaydzhan
U. Western Cis-Caucasus
V. Emba
W. Western Siberia
X. Volga-Ural Area
Y. Baltic Area
Z. Eastern Siberia

juvenile petroleum in the light isotope (Orovician - δC^{13} = -3.11 percent; Silurian - δC^{13} = 3.03 percent; Devonian - δC^{13} = -3.01 percent; Mississippian - δC^{13} = -2.99 percent; Pennsylvanian - δC^{13} = -2.94 percent; and Permian - δC^{13} = -2.82 percent). T. A. Botneva, P. Muller, and R. Glogochevskiy noted that the data they obtained on Tertiary crude oils of the Cis-Caucasus, the Carpathian Flysch (Polish People's Republic), Zechstein (German Democratic Republic), and Cambrian-Silurian of the Baltic Area indicate the dependence

of the isotopic composition on age, analogous to the dependence shown by J. Hunt and E. Degens.

Generally speaking, a correlation between the isotopic composition of carbon in crude oils with their geologic age, more exactly with the age of the country rock, must be approached cautiously. /133 As we know, even establishing any age dependences between coals and carbonates requires thousands of determinations. But crude oils, in contrast to other minerals, are subject to broad migration.

It should also be noted that thus far no fractors are yet clear that could account for the regular variation in the isotopic composition of crude oils profilewise. Study of these relationships for carbonates shows that regular variations in the isotopic composition do exist, however the variations did not change monotonely with time [29]. If one links the variation in the isotopic composition of crude oils with the features of the evolution of the biosphere, then it is strange that this tendency is clearly absent in coals. Moreover, as shown by investigations we conducted jointly with A. B. Ronov and A. M. Migdisov, variation in the isotopic composition of diffuse organic matter and bitumenoids for Russian Platform) is not at all characterized by a smooth increase in the content of the light isotope from the more juvenile to the more ancient deposits. If the variation in the isotopic composition of crude oils is linked to the degree of their transformation, it is typical to imagine the mechanism for the enrichment of the more ancient crude oils in the light isotope. The enrichment of crude oils in the heavy isotope resulting from many secondary processes is also highly problematical, but here at least general considerations are possible, for example, the dissipative loss of light fractions, cleavage of isotopically light low-molecular hydrocarbons, and so on.

Within particular regions the dependence of the isotopic composition on age is much more complicated. Thus, in the crude oils of the Permian Ural Area we investigate , the most isotopically light crude oils relative Riphean deposits, Devonian crude oils are heavier, and Carboniferous crude oils are again isotopically light. The Lower, Permian crude oils are even more enriched in the light isotope. In addition, the δC^{13} values of crude oils belonging to deposits of various stages of this same system are grouped around mean values sometimes markedly differing from each other. For example, Visean crude oils average 0.15 percent enrichment in the light isotope relative to Turonian crudes of the Lower Carboniferous, while Famennian petroleum is isotopically lighter than Franconian petroleum of the Upper Devonian.

When the crude oils of the Permian Ural Area and the Permian Basin of the United States were compared, it was found that Predevonian crude oils have approximately identical isotopic composition (-3.02 and -3.05 percent, respectively [184]), but higher

along the profile the nature of the variation in isotopic composition markedly changes. Common to both is only the fact that on the average Paleozoic crude oils of the same area are characterized by approximately the same range of δC^{13} values, with a mean close to -2.9 percent, markedly differing in this respect from Tertiary crude oils, for example, of California or Sakhalin, for which on the average δC^{13} values are close to (-2.4) - (-2.5 percent).

Thus, there hardly is a regular variation in the isotopic composition of crude oils with geologic age, as was assumed by J. Hunt and E. Degens. It appears more substantial that crude oils belonging to a given region (oil-gas-bearing basin) are characterized by relative constancy of isotopic composition. Actually, the isotopic composition of crude oils from 52 deposits in the Permian Ural Area are bounded by a δC^{13} range from -2.65 to -3.05 percent. Investigation of the isotopic composition of crude oils from several deposits in Tyumenskaya Oblast in Western Siberia (Samotlorskoye, Megionskoye, Aganskoye, Var'yeganskoye et al.) showed that crude oils of the Lower Cretaceous and Upper Jurassic complexes are among the isotopically light crude oils, where the δC^{13} values ranges from -3.00 to -3.21 percent. The same narrow range of variations, as is clear from Fig. 31, is also characteristic of other regions. An exception is the region of the Cis-Caucasus, where according to the data of T. A. Botneva et al. [4], the crude oils are isotopically lighter than the crude oils we studied. /134

Thus, to the first approximation some unity of the isotopic composition of crude oils belonging to a specific oil-gas-bearing basin is observed. Probably, it is appropriate also to speak of a distinction between the mean isotopic composition of crude oils in productive complexes of ancient platforms, on the one hand, and productive complexes of Epihercynian platforms and zones of petroleum and gas accumulation adjoining regions of juvenile folding -- on the other, that is, to raise the question not in a geochronologic sense, but in a geotectonic sense. In order to be convinced of the nonrandom nature of the phenomena observed, we must accumulate considerable factual material from numerous oil-gas-bearing provinces of the world.

Research done thus far has touched mainly on total carbon in petroleum. However, since petroleum is not an individual compound, the isotopic composition of its total carbon conveys limited information. In it are averaged variations of the isotopic composition of numerous individual hydrocarbons that have different chemical histories. A new step in the geochemical study of petroleum can be made along the path of a more detailed investigation of the isotopic composition of individual hydrocarbons and fractions of crude oils, and on this basis -- a more detailed comparison of the distribution of isotopes in constituents of petroleum and organic matter.

The foreign literature has a number of reports about the isotopic composition of carbon in petroleum constituents. It was noted that aromatic hydrocarbons are isotopically heavier than methane hydrocarbons [198, 220]. Asphaltenes and tars are enriched in C^{13} compared with petroleum overall [219]. Enrichment of solid paraffins in the light carbon isotope was noted. These results however are poorly comparable, since different constituents in different crude oils were studied, and by different investigators. Moreover, the reports are limited and they are often qualitative in nature.

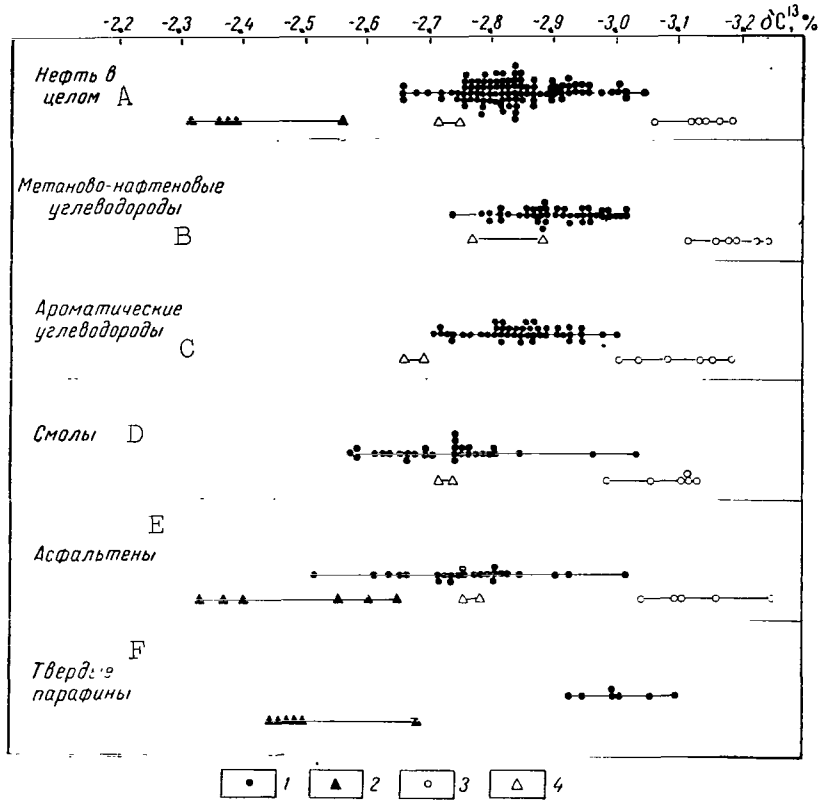


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Fig. 32. Isotopic composition of carbon in constituents of petroleum from different regions
1. Permian Ural Area (Paleozoic)
2. Northern Sakhalin (Myocene)
3. Western Cis-Caucasus (Tertiary) [4]
4. As above (Cretaceous) [7]

Key: A. Petroleum overall
B. Methane naphthenic hydrocarbons
C. Aromatic hydrocarbons
D. Tars
E. Asphaltenes
F. Solid paraffins

Since 1967, in our laboratory investigations have been underway, financed by the Permneft' Association (chief geologist, S. N. Vinnikovskiy), on the isotopic composition of crude oils and gases of deposits in the Permian Ural Area (Northeastern part of the Volga-Ural oil-gas province); the research program provides for analyzing narrow-temperature fractions and constituents of crude oils. Analyses of the isotopic composition of crude constituents were begun simultaneously with us by T. A. Botneva in collaboration with GDR /136
scientists P. Mueller, R. Winholtz, and others at the mass-spectrometry laboratory of the Leipzig Institute of Stable Isotopes (J. Maas, R. Birkenfeld, et al.) (Fig. 32).

The isotopic composition of carbon in various crude oil constituents will be examined in the following sections more concretely and in greater detail. Even from a generalized graph it is clear that the isotopic composition of carbon of the isolated constituents is dissimilar. Aromatic hydrocarbons on the average contain isotopically heavier carbon than methane-naphthenic hydrocarbons (paraffinic-naphthenic). True, in narrow petroleum fractions, as will be shown, the ratio can be the reverse. Tars and asphaltenes in the crude oils of the Permian Ural Area are enriched in the heavy carbon isotope by an average of 0.15 percent relative to total carbon in the crude oil. A similar enrichment in C^{13} of tars and asphaltenes, with a small exception, is characteristic of each crude oil considered separately. As a rule, in the crude oils of the Western Cis-Caucasus [4], tars are enriched in the heavy isotope relative to total carbon in the crude oil, while asphaltenes behave differently: in Mesozoic crude oils they are isotopically lighter, while in Tertiary -- heavier than the total carbon of the crude oil. In the Miocene crude oils of Northern Sakhalin enriched asphalt-tar constituents were analyzed together, sometimes a different ratio between the isotopic composition of total carbon in the crude oil and the carbon in the asphalt-tar portion was also observed (Table 35). High-molecular solid paraffin in the crudes of the Permian Ural Area and Northern Sakhalin are relatively enriched in the light carbon isotope.

The statistical comparison made in Fig. 32 is useful in that /137
it reveals characteristic features of the distribution of carbon isotopes in the components of various crudes. For example, variations in the carbon isotopic composition in the constituents of the same crude, or to put it a better way, in the constituents of crudes belonging to the same producing complex, are significantly smaller than differences in the isotopic composition of different crudes. Curves of the constituent-based distribution of carbon isotopes in different crudes are apparently shifted parallel to each other. Thus, the isotopically heaviest of the Miocene crudes of Sakhalin shown in the graph (Fig. 32) also contain the heaviest asphalt-tar constituents and isotopically heavy paraffin, though the latter represents in the Sakhalin crude oils as such, as in other cases, the isotopically lightest constituent. The same is

TABLE 35. ISOTOPIC COMPOSITION OF UPPER MIOCENE CRUDES FROM NORTHERN SAKHALIN (SAMPLES OF N. B. VASSOYEVICH)

Deposit	Bore hole nr	Stratum	Interval, m	Specific gravity ρ_4^{20}	δC^{13}, ‰			
					Petroleum	Oil fraction	Tars + asphaltenes	Solid paraffin
Central Sabo	43	VII	1222—1240	0.9263	—2.32	—2.30	—2.33	—2.47
As above	42	XX	2020—2044	0.8474	—2.56	—2.61	—2.56	—2.50
Kydylan'i	10	VII	1432—1438	0.8668	—2.37	—2.50	—2.37	—2.47
Tungor	6	XI	2128—2138	0.8419	—2.38	—2.32	—2.65	—2.45
"	118	XX	2076—2125	0.8474	—	—2.54	—2.61	—2.68
Pil'tun	18	II	449—459	0.8395	—2.38	—2.44	—2.40	—2.48

characteristic of Mesozoic and Tertiary crudes of the Cis-Caucasus. T. A. Botneva, P. Mueller, and J. Maas observed: "In the Mesozoic crudes that have a heavier isotopic composition of carbon, the carbon is also heavier in all fractions. In Tertiary deposits total carbon and the carbon of all fractions is lighter" [4].

This parallelism in the isotopic composition of carbon in the individual constituents to a large extent does away with a relationship between the isotopic composition of total carbon and the quantitative ratio of constituents in crudes.

Geological Factors Determining Isotopic Composition of Petroleum. Problems of Formation of Pools

Factors of Migration. Seismic Factor in Migration and Accumulation of Petroleum

By involving carbon isotopy in petroleum and gas in the discussion of the problem of pool formation, one must first of all turn to the possible mechanisms of the mobilization and accumulation of hydrocarbons. This complex problem has not yet found satisfactory solution. We have formed a certain conception of the driving forces of primary migration. The main role in this process, in our view, is a factor that can be called the seismic factor. Here it is appropriate to discuss this somewhat, since in the following when we deal with the questions of pool formation we will start from our understanding of the mechanism of primary migration, accumulation, and dispersion of hydrocarbons.

An extensive literature deals with primary migration, and we cannot delve into a detailed analysis.

Initially, it was assumed that sedimentary consolidation and, /138 in some cases, tectonic compression of rocks led to the release of hydrocarbons together with the water squeezed out into a reservoir in which they accumulated in the pool through forces of gravitational surfacing. The movement of hydrocarbons here was assumed to be in the liquid-droplet state. However, it was found that adsorption and capillary forces restraining hydrocarbons in rock considerably exceed the possible value of the constituent of the forces of hydrostatic or tectonic compression.

Experiments on consolidated rocks and artificial samples in static compression devices showed that under conditions simulating natural pressures and concentrations of hydrocarbons in rock only water is squeezed out.

The low phase permeability of dispersed hydrocarbons given the actual coefficients of their saturation of the pore space of petroleum-parental rocks led to the idea that their primary migration occurred chiefly in the water- or gas-dissolved state (V. A. Uspenskiy, 1954; I. B. Vassoyevich and S. A. Radchenko, 1955). It was shown that at high gas pressures (CO_2, CH_4, and so on) petroleum hydrocarbons are capable of being dissolved, including high-molecular hydrocarbons all the way to tarry substances (M. A. Kapelyushnikov, T. P. Zhuze, M. I. Gerber, and S. N. Beletskaya). However, when the experimental conditions were transferred to natural conditions, it turned out that the required volumes of gases considerably exceed the gas-generating capabilities of sedimentary rocks. Moreover, for a detectable dissolving of high-molecular constituents, as a rule pressures were required that exceeded 400-600 kg/cm^2, while numerous oil deposits are formed at depths of 1500-2000 m (that is, at pressures of 150-200 kg/cm^2). Actually, the process of hydrocarbon generation occurs in water-saturated rock. It was assumed that the presence of gas increases the solubility of the hydrocarbons in water. However, recently experiment proof was obtained that increasing the gas content in water leads to a reduction in the solubility of liquid hydrocarbons [92].

In pure water, gaseous and liquid hydrocarbons have low solubility. The solubility considerably increases in the presence of a number of surface-active compounds, salts of fatty acids (soaps). On this basis, in several studies the idea of the micellary mechanism of primary migration and accumulation of petroleum was advanced (M. F. Dvali, E. Baker, W. Meynstein, and W. Kennedy). However, analyses of the content in subsurface waters of compounds promoting micelle formation showed that their concentration is very low. The substantial difference in the critical concentration of micelle formation for salts of high-molecular fatty acids, of the order of

1000 mg/liter, and their actual concentration in water, 10 mg/liter, /139 casts doubt on the broad significance of the mechanization of hydrocarbon migration in the water-dissolved state [92].

The idea of petroleum migrating in the form of true solutions or by the formation of water-soluble complexes brought up a new problem -- the necessity of explaining the reverse release of water-dissolved hydrocarbons. Here there are also considerable difficulties (H. Hobson, 1961; U. Colombo, 1967).

The impression is given that the ideas of hydrocarbons migrating in the water- or gas-dissolved state has weaknesses that limit the capabilities of a comprehensive explanation, on this basis, of the actual process of hydrocarbon migration and accumulation. This made it necessary to re-examine the mechanism of primary migration in the droplet-liquid state. T. P. Zhuze et al. [92] suggested that a promising mechanism can be the one of the transport of hydrocarbons in the form of a finely dispersed emulsion. The size of a xylene-water emulsion droplet experimentally found in a study cited by these investigators, is 0.02-0.04 micron, which is less than the size of pores in clay rocks. But in this case again there arises the question of the mechanical forces capable of overcoming the molecular and surface forces of cohesion, paralyzing the mobility of hydrocarbons dispersed in rock pores.

It should be borne in mind that the mechanism of the primary migration of hydrocarbons must have a sufficiently general character, since oil-gas accumulation is an extremely widespread phenomenon in nature. But, on the other hand, oil pools are not encountered everywhere. Sometimes they are absent over very large territories.

Any phenomenon of a nonubiquitous nature must contain a certain restraint. From the standpoint of the chemical aspect of petroleum formation, this restraint must be regarded as the attainment by the organic matter of a certain stage of transformation. But this is not sufficient. This restraining factor must be contained in the mechanism of the primary migration and accumulation of hydrocarbons.

Subsurface water, according to the calculations of V. M. Shvets [114], contains $2.5 \cdot 10^{12}$ tons of organic matter. This is commensurable with the size of the world's petroleum reserves ($1.5 \cdot 10^{12}$ tons, according to N. B. Vassoyevich). And this figure reflects the ongoing concentration of organic matter in water, kept at a certain level of even three orders greater than the reserve of the organic matter in rocks ($3.5 \cdot 10^{15}$ tons). At these ratios, it appears acceptable from the quantitative point of view that petroleum was formed directly from organic matter contained in stratal water. All the more so is this true in that stratal waters (except for petroleum deposits) have a noticeable amount of high-molecular fatty acids, naphthenic acids, phenols, that is, compounds that are extremely similar structurally to petroleum hydrocarbons. If /140

the latter are then formed, their accumulation obviously does not occur. Otherwise the territorial distribution of crude oils would be regular, since the content of the same naphthenic acids (1.9 mg/liter) and phenols (1.1 mg/liter) in groundwater and in the water of nonpetroleum-bearing artesian basins is only slightly less than in the subsurface water of petroleum-gas deposits (0.5-0.6 and 0.6-3.0 mg/liter, respectively) [114]. In other words, a given accumulation of petroleum must have been contained in each appropriate trap of any region. Since this does not occur, this means that the dispersed hydrocarbons formed in this way in a reservoir were able to be concentrated and removed from the interior with subsurface water through the regions of their unloading. This must exactly be the fate of hydrocarbons migrating into a reservoir from the petroleum-parent deposits if they are arriving continuously.

Obviously, processes of generation and dissipation on the average are balanced out and only an abrupt increase in the influx of hydrocarbons over a short time interval can lead to their accumulations being formed. To put it briefly, the emigration and accumulation of hydrocarbons necessitates some special circumstances. We find these special circumstances, corresponding at the same time to the condition for broad geologic distribution, in the manifestation of tectonic activity. But we direct attention not to the large-scale of manifestations of tectonism, not to the consequences of its more or less prolonged action, such as changes in the structural plan or hyposometric position of deposits, changes in the textural characteristics of rocks (consolidation and fissuring), the composition and hydrodynamics of subsurface water, and so on, but to the momentary manifestation of tectonic activity expressed in seismic vibrations. In Recent seismically active regions, vibrations of soil are recorded virtually continuously. For example, for a period of ten years the number of earthquakes with magnitude $M > 5$ in the Southern California was 10, with $M \geqslant 4.0$ -- 115, with $M \geqslant 3.0$ -- 832, and so on (V. Gutenberg and C. F. Richter, 1961). There is an empirical relationship between the frequency of earthquakes N and their magnitude. In particular, for this region it has the following form: $\lg N = 4.77 - 0.85 M$. Therefore, in seismically active regions the number of earthquakes including weak earthquakes ($M \geqslant 1$), is 10^4 year^{-1}. It should be noted that this figure characterizes a generally moderate seismic region. Thus, whereas in Southern California not a single earthquake with magnitude exceeding 7.5 was recorded for ten years, in Japan there were 14 earthquakes with $M \geqslant 8$ in the period 1897-1907 alone.

The mechanism of the action of seismic vibrations is analogous to the action of "shaking". Just like friction-coalesced sandstones do not slide fast the holes of a fixed sieve, but are screened completely when shaken, dispersed hydrocarbons move in rock through /141
seismic vibration, instantaneously freed from the cohesive forces of capillary or sorptional nature.

We undertook the following experiment (the experiment was conducted by study Yu. Krasavin as part of his course project, 1969). Two samples of a core of aleurolitic sandstone with 6 and 12 percent porosity were completely dehydrated by heating in vacuum and were saturated with kerosene. Then, using a semipermeable membrane, the kerosene was displaced with water. The fraction of the kerosene remaining in the sample did not yield to further displacement with water, that is, its phase permeability at the given coefficient of "petroleum saturation" was zero. Then the device containing the core was placed on a vibratory table, where it was kept 8 hours, as a vibration frequency of 20 sec^{-1} and an amplitude of 0.05 cm. As a result, further an approximately 80 percent of the kerosene remaining in the cores was separated. If one takes note of the data on the nature of vibrational motions in seismically active regions, it is easy to calculate that this vibratory treatment corresponds to a residence in conditions of this region for approximately 5000-10,000 years.

There are reports of the actual manifestation in nature conditions of the action of a seismic factor mobilizing hydrocarbons. A. Levorsen [78] presents an example where as a result of the Tehachi-Bakersfield earthquake in California in 1953, the recovered petroleum was doubled for several weeks at one of the deposits near Mountain View. Several geologists noted the possible effect of earthquakes on the nature of subsurface fluids, including on the migration of hydrocarbons. Data have been presented indicating a relationship between oil-gas-bitumen manifestations and neotectonic movements [70, 87, 112] -- usually in confirmation of considerations of possible vertical vibration (fault opening). A. Levorsen assumed that changes in stratal pressure caused by tidal perturbations or fluctuations in atmospheric pressure, that is, microseisms, can promote processes of petroleum migration and accumulation [78].

It should be stressed that we do not identify the seismic factor either with earthquakes reflecting a more narrow concept, nor with microseisms, acting everywhere and at all times. But the important thing, as it appears to us, is that the seismic factor must be viewed not as promoting, but as determining the actual possibility of hydrocarbons migrating and accumulating.

It is precisely with this approach that certain problems take on a satisfactory interpretation.

1. A unity is achieved between the mechanism of primary migration and the accumulation of hydrocarbons. There is no longer any necessity to link two processes that are analogous in their /142
essentials in one case with the forming up solutions, and in another case with breakdown. The form of material most appropriate for migration is minute droplets or particles. However, the significance of the bond system water -- petroleum -- gas in the migration mechanism obviously is also large and above all in as far as the extractive

action is involved. The transporting role of gas possibly consists not in the formation of a gas solution, but in the mechanism like flotation.

2. In accordance with the principle developed here, formation of accumulations requires that the continuous generation of hydrocarbons not be accompanied by their continuous release into a collector-stratum. Accordingly, added importance is gained by the capacity of petroleum-parent rocks not only to generate hydrocarbons, but in contrast to reservoirs, to retain them in tectonically quiet periods and to intensively release them into a reservoir under the action of seismic shaking. The avalanche-like passage of diffuse hydrocarbons into a collector and rapid movement therein owing to the same seismic mechanism leads in a short period of seismic activity to the formation of oil-gas lenses. The latter, exhibiting a continuous phase, move through the stratum and, on reaching the traps, form and build up a pool.

Hydrocarbons, which for various factors (for example, owing to the sedimentational consolidation of clays, and segregation in the form of a gas solution) pass from petroleum-generating rocks into the collector in the form of a constant, but extremely rarefied flow, just like hydrocarbons formed in the reservoir itself remained in the diffuse state, producing a hydrocarbon background of stratal water, and are removed through the movement of subsurface water through regions of unloading.

A simple calculation shows that if the principal phase of petroleum formation lasts, for example, ten million years, then when there is a continuous release of hydrocarbons the flow considered per kg of parent rock when the mean content of organic matter in the rock is 20 g/kg and the degree of its transformation into hydrocarbons is 25 percent will be $0.5 \cdot 10^{-6}$ g/kg·year. At the maximum rate of flow of subsurface water of 0.1 cm/year and the mean solubility of hydrocarbons in water of 10 mg/liter, the hydrocarbon flow carried by subsurface water through unloading regions will be 10^{-3} g/liter·year. Therefore, the hydrocarbon flow from petroleum-parent rocks must have an intensity that is tens of thousands of times greater than its mean value in order for the hydrocarbons be able to accumulate in the reservoir. In our example this means that during the entire period of petroleum generation the time involved in the periods of petroleum release altogether does not exceed a thousand years.

It is possible that the property of petroleum-parent rocks to accumulate hydrocarbons and intensively release them into a reservoir, more than any other factor, determines their petroleum-producing significance in the profile. The increased content of organic /143
matter or the large catalytic activity of clays does not have as fundamental an importance.

3. Since seismic vibrational motion encompass the entire volume of sedimentary rocks deposited by the period of the given tectogenesis, obviously deformation of pools (when appropriate conditions are present in the sense of the content and degree of the transformation of the organic matter) must occur over the entire cross section simultaneously. In our view this best explains why in some regions the entire profile is productive to some extent, and in others there are no productive horizons.

N. A. Kudryavtsev formulated this problem as follows: "The multistage nature of petroleum and gas deposits, along with the confinement of petroleum-bearing provinces to deep fissures, is their characteristic feature, quite inexplicable from the standpoint of organic theory. Therefore over a series of geological periods and even eras, the formation of petroleum from organic matter was confined to specific provinces exhibiting definite features of tectonic, but sharply different from each other in composition, very nature, and the conditions of the accumulation of petroleum-bearing deposits, where over the extent of geologic time the composition of the latter changed no less abruptly in nearly each of these provinces -- this is entirely incomprehensible" [71]. Usually the presence of petroleum in many horizons of the same deposit is accounted for by the processes of vertical migration. But the results of isotopic analysis of petroleum show that pools relating to different stratigraphic complexes contain petroleum of different genetical types [49].

4. The role of seismicity as a factor in the emigration of hydrocarbons and in the formation of pools is in agreement with the certain confinement of oil-gas-bearing provinces to tectonically mobile geostructural elements. The marginal areas of a platform involved in the geosynclinal process are seismically active zones during the corresponding tectonic cycle. In the internal parts of the platform the oil-gas-bearing provinces can be formed on the basis of aulakozens or structures inversional with respect to them. Seismic activity in platforms can be caused by magmatic activity, for example, by the forming of a trap formation. Local petroleum manifestations are possible as part of the formation of intrusions, including dikes and kimberlite pipes. Seismicity of a local nature must accompany the growth of salt domes. A. Levorsen wrote: "The development of salts domes can account only for the formation of traps, but not for the origin of pools" [78].

If we bear in mind local seismicity that can be responsible for the growth of a salt dome, we state that the buildup of salt domes accounts not only for the formation of traps, but also for the origin of salt-dome deposits. Similarly, the petroleum manifestations in rocks adjoining kimberlite pipes that caused a quandry are thus explicable, in the absence of signs of oil-gas presence in the corresponding deposits removed from the pipes. /144

The formation of troughs as a rule, transected by bedrock faults it is also obviously not limited to the formation of favorable structural traps, but simultaneously owing to the accompanying tectogenesis of seismicity leads to the mobilization of hydrocarbons and pool formation.

Thus, the relationship between oil deposits and tectonically active provinces and deep faults as well as the localization of petroleum manifestations in the zone of intrusion into the sedimentary casing of intrusive formations and salt stocks noted by several investigators and often polemically linked to the chemical history of petroleum and to its inorganic origin, in our view is a natural manifestation of the characteristic kinematic mechanism of oil pool formation.

N. B. Vassoyevich et al. [10] formulated a historico-geologo-geochemical method of estimating the promise of sedimentary basins as to petroleum and gas: "Essentially, the method boils down to determining the petroleum-producing potential of rocks deposited in a given sedimentary basin. First of all, strata with increased content of organic matter are singled out, especially of the type capable of generating hydrocarbons. Next, the level of catagenetical transformation of rocks is determined. From the point of view of petroleum and gas presence, most promising is the section of the petroleum-parental strata that was at or is at the level of the mean catagenesis, when coalification of the organic matter corresponding to coals of grades D, G, and Zh occurred. Some of the petroleum-parental layers that are still in the stage of early catagenesis are capable of generating only gas, that is, they do not participate in petroleum formation, and on reaching the stage of transformation above the mean stage, now their petroleum-generating capabilities are realized, and its Recent role amounts only to the generation of gas. Essential for the formation of oil pools is that the traps be formulated before the principal phase of petroleum formation or, at least, before its culmination."

In light of the foregoing, this complex of prognisticatory features, in our view, must be supplemented by an indication of the specific source of seismicity active in the period of the principal phase of petroleum formation.

Abundance of Carbon Isotopes in Petroleum Areally and Profilewise in the Petroleum Province. Genetical Types of Petroleum

The isotopic composition of petroleum carbon was analyzed in detail in deposits of a large region, including the eastern end of the Russian Platform and part of the Cis-Ural Trough, territorially bounded by Permskaya Oblast and adjoining regions. The main tectonic elements of this region include the Kamskiy anticline in the /145

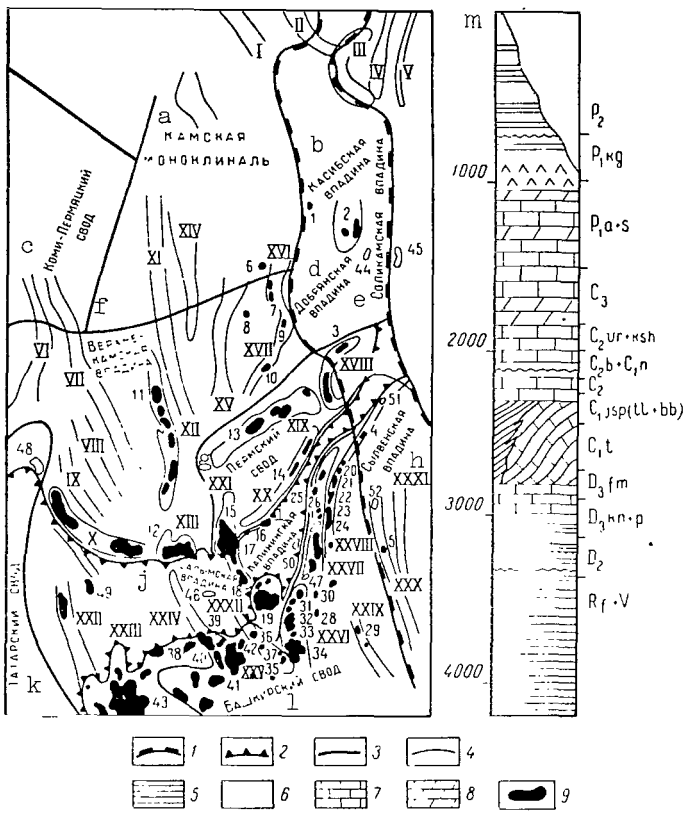

Fig. 33. Tectonic scheme, normal profile, and location of petroleum deposits studied in Permskaya Oblast and adjoining regions of Udmurtiya, Tatariya, and Bashkiriya.

Tectonic elements of second order:
I. Kel'tmenskiy swell
II. Ksenofontovo-Kolvinskiy swell
III. Polyudovskaya anticlinal zone
IV. Govorukhinsko-Nemydskaya anticlinal zone
V. Belgursko-Berdyshkaya anticlinal zone
XIII. Nozhovskiy structural bench, swells:
VI. Neopol'skiy
VII. Kuliginskiy
VIII. Debesskiy
IX. Zurinskiy
X. Kiyengopskiy
XI. Kochevskiy
XII. Vereshchaginskiy
XIV. Kudymkarskiy
XV. Voskresenskiy

/Caption to Fig. 33, concluded/

XVI. Maykorskiy
XVII. Vasil'yevskiy
XVIII. Yarino-Kamennolozhskiy
XIX. Krasnokamsko-Polaznenskiy
XX. Lobanovskiy
XXI. Osinskiy
XXII. Andreyevskiy
XXIII. Ivanayevskiy
XXIV. Kuyedinskiy
XXV. Dubovogorskiy
XXVI. Chernyshinskiy
XXVII. Mazuninskiy
XXVIII. Veslyanskiy
XXIX. Dorokhovskiy
XXX. Tulumbasovskiy
XXXI. Berezovskiy
XXXII. Batyrbayskiy bench. Deposits and exploratory areas investigated (numbers in scheme):

1. Kasibskoye
2. Durinskoye
3. Ol'khovskoye
4. Komarikhinskoye
5. Brusnyanskoye
6. Tukachevskoye
7. Maykorskoye
8. Romanshorskoye
9. Chermozskoye
10. Kuz'minskoye
11. Sivinskoye
12. Nozhovskoye
13. Krasnokamskoye
14. Kozubayevskoye
15. Osinskoye
16. Rassvetovskoye
17. Yelpachikhinskoye
18. Tulvinskoye
19. Batyrbayskoye
20. Yelkinskoye
21. Ozhginskoye
22. Kylasovskoye
23. Yergachinskoye
24. Luzhkovskoye
25. Kukushtanskoye
26. Lazukovskoye
27. Troyel'zhanskoye
28. Tartinskoye
29. Dorokhovskoye
30. Aspinskoye
31. Krasnogorskoye
32. Severo-Tanypskoye
33. Tanypskoye
34. Pavlovskoye
35. Etyshskoye
36. Dubovogorskoye
37. Stepanovskoye
38. Gozhanskoye
39. Byrkinskoye
40. Gondyrevskoye
41. Kuyedinskoye
42. Aryazhskoye
43. Arlanskoye
44. Yayvinskaya area
45. Vsevolodo-Vil'nevskaya
46. Bezymyannaya
47. Kuliginskoye
48. Krasnogorskaya
49. Gremikhinskoye
50. Byrminskaya area
51. Kopal'ninskaya area
52. Tazovskaya

1-4. boundaries of Cis-Ural Trough, Kamsko-Kinsel'skaya Depression, and tectonic elements of I and II orders
5. clays
6. aleurolites
7. limestones
8. dolomites
9. deposits

KEY:

a. Kamskaya Monocline
b. Kasibskaya Depression
c. Komi-Permyatskiy Arch
d. Dobryanskaya Depression
e. Solikamskaya Depression
f. Verkhne-Kamskaya Depression
g. Permskiy Arch
h. Sylvenskaya Depression
i. Kalininskaya Depression
j. Shalymskaya Depression
k. Tatarskiy Arch
l. Bashkirskiy Arch

north, the Verkhnekamskaya depression in the west, by the Permsko-Bashkirskiy anticline separated from the Tatarskiy anticline by the Birskaya saddle, in the south, and also by the Solikamskaya and Yurezano-Sylvenskaya depression within the Cis-Ural Trough (Fig. 33).

The commercial petroleum bearing status of a province is associated with productive horizons in the strata of the Devonian, Carboniferous, and Permian. Heavy petroleum manifestations are established in Predevonian (Upper-Proterozoic) strata.

Table 36 gives the mean δC^{13} for carbon in the crude oils of the investigated pools of Permian Ural Area deposits. N. G. Kuznetsova showed that the isotopic composition of the carbon in crude oils of a hydrodynamically single productive horizon, sampled from different boreholes and at different times varies very slightly, differing in this respect from gases, in whose different samples taken sometimes from the same pool noticeable isotopic shifts are observed.

All deposits in which crude oils of Permian strata (Artinskiy and Sakmarskiy stages) were investigated, lie within the Cis-Ural Trough. Intervening deposits are represented chiefly by carbonate rocks -- limestones and dolomites. Characteristic of the limestones is their organogenic origin and reef disposition. Above, in strata of the Kungurskiy Stage, and in the platforms -- in the Artinskiye strata -- sulfates are observed -- mainly anhydrides. The depth of the deposits studied is 950-1600 m.

There is a certain correlation between change in isotopic composition of Permian crude oils distributed along the Cis-Ural Trough. The isotopically lightest crude oil was found in the Durinskoye Deposit (δC^{13} = -3.02 percent). To the south of it the crude oils are gradually enriched in C^{13}: Golubyatskoye Deposit -- $\delta C^{13} = -2{,}96\%$, Kapal'ninskoye Deposit $\delta C^{13} = -2{,}90\%$, Komarikhinskoye Deposits -- $\delta C^{13} = -2{,}86\%$. . Deposits to the north of the Durinskoye Deposit are also enriched in C^{13}. Vsevolodo-Vil'venskoye -- $\delta C^{13} = -2{,}84\%$, and Yaborovskoye $\delta C^{13} = -2{,}83\%$.

A comparison of the isotopic composition of crude oils with parameters characterizing crude oil properties and bedding conditions (see Table 36) shows that there is no corresponding relationship.

The middle Carboniferous productive complex embraces the Kashirskiy and Vereyskiy productive horizons of the Moscovian Stage and the productive strata of the Bashkirskiy stage. They include the Namyurskiye crude oils of the Lower Carboniferous, forming as a rule general Namyursko-Bashkirskiy deposits. Carbonate rocks serve as the reservoirs.

TABLE 36. MEAN ISOTOPIC COMPOSITION OF CARBON IN PETROLEUM FROM DEPOSITS OF THE PERMIAN URAL AREA

Deposit (area)	Stratigraphic complex	Depth, m	Country rock	Density, g/cm³	Content % Sulfur	Asphaltenes	Tars	δC^{13}, ‰
1	2	3	4	5	6	7	8	9
Komarikinskoye	P_1a	945	Carbonate	—	—	—	—	−2.86
»	C_2vr	1603	»	—	—	—	—	−2.84
»	C_1tl	1950	Terrigenic	0.781	0.51	abs.	3.07	−2.76
»	C_1t	2053	Carbonate	0.805	1.10	»	5.03	−2.66
Ozhginskoye	C_2b	—	»	—	—	—	—	−2.72
»	C_1jsp	1620	Terrigenic	0.8328	0.39	0.04	6.29	−2.68
Durinskoye	P_1a	—	Carbonate	0.8263	0.71	0.21	6.64	−3.02
»	C_2t	1951	»	0.8405	0.67	0.66	9.36	−2.84
»	C_2b+C_1n	1925	»	0.8633	0.76	1.10	11.68	−2.87
»	D_3fm	2131	»	0.8396	0.72	1.40	9.58	−2.98
Osinskoye	C_2b	1029	»	0.8733	2.34	2.60	11.99	−2.90
»	C_2n	1431	»	0.8668	2.27	2.62	8.92	−2.91
Gondyrevskoye	C_2b	989	»	0.8831	2.24	—	—	−2.78
»	C_1t	1310	Terrigenic	—	—	—	—	−2.84
»	C_1bb	1321	»	—	—	—	—	−2.76
»	C_1t	1339	Carbonate	0.8861	2.44	2.96	21.07	−2.77
Nozhovskoye	C_1tl	1525	Terrigenic	0.9054	3.27	4.63	20.08	−2.88
»	C_1jsp	1541	»	0.8947	3.01	3.63	19.20	−2.91
Tulvinskoye	D_3p	2123	»	0.9042	2.67	7.45	26.36	−2.80
Romanshorskoye	C_1bb+tl	1770	»	0.8972	2.11	—	—	−2.94
»	C_1jsp	1770	»	0.9105	2.21	9.39	20.37	−2.87
Rusakovskoye	C_1tl	1772	»	0.8442	1.02	0.78	11.86	−3.02
Tartinskoye	C_1tl	1458	»	0.8589	1.45	—	—	−2.81
Dorokhovskoye	D_3fm	2110	Carbonate	0.8810	1.84	2.54	15.10	−2.80
Chermozskoye	C_1bb	1836	Terrigenic	0.8942	2.27	—	—	−3.01
Vsevolodo-Vil'venskoye	P_1s	1600	Carbonate	0.8091	0.40	—	—	−2.84
Severo-Tanypskoye	C_1t	1541	»	0.8736	2.13	—	—	−2.84
"	C_1tl	1427	Terrigenic	0.8780	1.97	—	—	−2.80
Kuligинskoye	C_1tl	1604	»	0.8598	1.18	—	—	−2.78
"	D_3kn+p	2279	»	0.8955	1.94	—	—	−2.81
Krasnokamskoye	C_2b+vr	1124	Carbonate	0.8493	1.08	1.74	7.04	−2.93
»	D_3	1725	Terrigenic	0.8456	0.64	2.71	10.79	−2.84
Konstantinovskoye	$C_2vr+ksh$	1069	Carbonate	0.8808	2.05	3.72	15.47	−2.78
Yergachinskoye	C_1tl	—	Terrigenic	—	—	—	—	−2.66
Batyrbayskoye	C_2b	1124	Carbonate	0.8754	2.27	3.17	15.27	−2.85
»	C_1tl	1410	Terrigenic	0.8838	2.51	4.30	14.29	−2.92
Pavlovskoye	C_2vr	1045	Carbonate	0.8634	1.78	1.91	11.25	−2.76

TABLE 36 /CONCLUDED/

Deposit (area)	Stratigraphic complex	Depth, m	Country rock	Density, g/cm³	Content % Sulfur	Asphaltenes	Tars	δC^{13}, ‰
1	2	3	4	5	6	7	8	9
Pavlovskoye	C_2b	1047	Carbonate	0.8823	2.30	2.83	15.28	—2.78
»	C_1tl	1402	Terrigenic	0.8813	1.98	4.37	11.14	—2.81
»	C_1bb	1423	»	0.9072	2.34	6.12	14.30	—2.80
»	C_1t	1444	Carbonate	0.9132	3.01	4.90	15.97	—2.80
Kopan'inskoye	P_1s	1080	»	0.8876	2.19	1.67	8.14	—2.90
Yaborovskoye	C_1t	1898	»	0.8039	0.09	abs.	1.82	—2.87
Kylasovskoye	C_2vr	1311	»	0.8862	1.14	3.40	9.50	—2.85
Yaborovskoye	P_1s	1002	»	0.8492	0.67	0.74	5.11	—2.83
Tsentral'naya	P_1a+s	577	»	0.8692	2.12	0.91	6.54	—2.83
Tanypskoye	$C_2vr+ksh$	1020	»	0.8696	2.16	2.66	12.61	—2.83
»	C_2b	1051	»	0.8768	1.99	3.06	9.55	—2.79
»	C_1tl	1433	Terrigenic	0.8749	1.84	4.15	12.32	—2.83
»	C_1bb	1421	»	0.8832	1.96	4.83	12.99	—2.82
»	C_1t	1462	Carbonate	0.8809	2.1	2.30	29.38	—2.81
Gremichinskoye	C_1jsp	1385	Terrigenic	0.904	2.63	2.07	22.54	—2.94
Yelkinskoye	»	1502	»	0.803	1.09	abs.	5.05	—2.93
Kuz'minskoye	»	1720	»	0.853	1.35	1.89	22.03	—2.85
Lazukovskoye	»	1758	»	0.908	2.33	3.74	15.72	—2.98
Luzhkovskoye	»	1612	»	0.858	1.91	0.78	10.02	—3.00
Ol'khovskoye	»	1838	»	0.815	0.54	—	4.75	—2.90
Stepanovskoye	»	1394	»	0.816	1.87	1.00	16.01	—2.87
Tukachevskoye	»	1715	»	0.874	1.63	3.02	14.55	—3.01
Troyel'zhanskoye	»	1694	»	0.862	1.78	1.46	9.38	—2.84
Yayvinskoye	»	2522	»	0.837	0.27	abs.	3.84	—2.92
Brusyanskoye	C_2b	1603	Carbonate	0.819	0.89	tr.	4.53	—2.84
Sivinskoye	»	1316	»	0.895	1.88	9.64	15.25	—2.93
»	Rf	2788	»	0.955	0.33	8.98	19.62	—3.05
Aspinskoye	C_1jsp	1501	Terrigenic	—	—	—	—	—2.78
»	D_3fm	1900	Carbonate	0.895	2.49	1.50	16.75	—2.70
»	D_3kn	2205	»	0.908	2.13	12.39	17.55	—2.78
»	D_3p	2203	Terrigenic	—	—	—	—	—2.84
Bezymyanskoye	D_3p	2220	»	0.939	2.68	5.82	24.94	—2.78
Platform								
Dubovogorskoye	»	2167	»	0.879	1.85	3.96	13.77	—2.84
Severokamskoye	»	1811	»	—	—	—	-	—2.95
Aryazhskoye	C_1t	1388	Carbonate	0.910	3.67	3.65	28.35	—2.77
Golubyatskoye	P_1a	945	»	0.951	3.18	5.93	11.85	—2.96
Etyzhskoye	C_1jsp	1329	Terrigenic	0.896	2.24	4.58	20.93	—2.85
"	C_1t	1388	Carbonate	0.930	3.55	8.44	24.25	—2.77
Rassvetovskoye	C_2b	1328	»	0.907	3.76	5.42	26.98	—2.81
»	C_1t	1716	»	—	—	—	—	—2.75
Kasybskoye	C_2b	1495	»	0.920	1.10	4.68	20.20	—2.95
»	C_1jsp	1770	Terrigenic	0.816	0.69	abs.	5.44	—2.89

/tr. = traces; abs. = absent/

The isotopic composition of Middle Carboniferous crude oils of Permskaya Oblast changes somewhat north to south. The isotopically lightest carbon is found for crude oils north and northeast /149 of the Permskiy anticline -- the deposits Kasipskoye ($\delta C^{13} = -2{,}95\%$) and Sivinskoye ($\delta C^{13} = -2{,}93\%$). Within the Permian Anticline, the isotopic composition of the Middle Carboniferous crude oils is characterized by $\delta C^{13} = -2.90$ percent (Osinskoye deposit). At the deposits adjoining the seven margin of the Kamsko-Kinel'skaya system, the Middle Carboniferous crude oils have $\delta C^{13} = -2.85$ percent (Batyrvayskoye and Kylasovskoye deposits). Finally, within the Permsko-Bashkirskiy Anticline, in the southern part of the province the Middle Carboniferous deposits contain the isotopically heaviest crude oils -- the deposits Tanypskoye ($\delta C^{13} = -2{,}80\%$), Pavlovskoye ($\delta C^{13} = -2{,}77\%$), and Gondyrevskoye ($\delta C^{13} = -2{,}78\%$). Thus, we observed a gradual isotopic weight gain in the crude oils of the Middle Carboniferous productive complex in the direction northwest to southeast.

The Visean terrigenic productive complex of the Lower Carboniferous includes the Tul'skiye and Bobrikovskiye petroleum-bearing horizons, united in the Yasnopolyanskiy complex. The crude oils lie in sand-clay deposits.

The area distribution of the isotopic composition of carbon in Visean crude oils is shown in Fig. 34. Also observed in the Visean complex is a tendency toward enrichment of crude oils in the heavy isotope, northwest to southeast. But here sometimes there coexist extremely isotopically light crude oil (Lazukovskoye deposit, $\delta C^{13} = -2{,}98\%$) and isotopically heavy crude oil (Yergachinskoye deposit, $\delta C^{13} = -2{,}66\%$). On examining the areal distribution of Visean crude oils of different isotopic composition, one can conclude that generally there occurs not the successive variation of isotopic composition in any particular direction, but the presence of two fields with different mean isotopic composition of crude oil carbon: a northwest field with crude oils whose isotopic composition varies from -2.85 to -3.02 percent ($\delta C^{13} = -2{,}92\%$), and a southeast field where the isotopic composition of the crudes varies from -2.66 to -2.85 percent ($\delta C^{13} = -2{,}79\%$).

The boundary between the northwest and southeast fields of distribution of Visean crude oils of different isotopic composition runs along the southern margin of the Kamsko-Kinel'skaya depression, where the boundary itself and several deposits along the southern margin belong to the northwest fields. Thus, for example, is the Batyrbayskoye deposit, which in terms of the isotopic composition of its crude oil is very close to the Osinskoye deposits lying along the southern margin of the Kamsko-Kinel'skaya depression. In the area of the Mazuninskiy and Veslyanskiy troughs, the

deposits Yelkinskoye , ($\delta C^{13} = -2{,}93$ percent), Lazukovskoye ($\delta C^{13} = -2{,}98$ percent), and Luzhkovskoye , ($\delta C^{13} = -3{,}00$ percent) belong to the northwest field, and the deposits Ozhginskoye ($\delta C^{13} = -2{,}72$ percent) and Yergachinskoye ($\delta C^{13} = -2{,}66$ percent) belong to the southeast field. Further, this boundary can be traced along the continuation of the Kamsko-Kinel'skaya system within the limits of the Cis-Ural Trough, where it divides the Ol'khovskoye deposit ($\delta C^{13} = -2{,}90$ percent) pertaining to the northwest field, and the Komarikhinskoye deposit ($\delta C^{13} = -2{,}76$ percent) which lies within the limits of the southeast field.

Tournaisian oil deposits are distributed over a smaller area /151 than the Visean deposits. Carbon of the Tournaisian deposits is characterized on the average by a noticeable enrichment in the heavy isotope. Here crude oils from deposits located within the Permian Anticline (Rassvetovskoye -- $\delta C^{13} = -2{,}75$ percent) and the Nozhovskiy dome ($\delta C^{13} = -2{,}77$ percent), that is, in the northwest field, have the same isotopic composition as crude oils from deposits of the southwest field (δC^{13} from -2.74 percent to -2.81 percent). The only studied deposits (Yaborovskoye) in the northern part of the Oblast, within the Solikamskaya depression of the Cis-Ural trough contains Tournaisian crude, characterized by $\delta C^{13} = -2{,}87$ percent, that is, isotopically much lighter than other Tournaisian crudes.

The Devonian productive complex is represented by terrigenic strata in the Kynovskiye and Pashiyskiye deposits of the Franconian stage, and also the Zhivetskoye and Eifelian stages. Deposits of the Franconian stage and two deposits among the carbonate deposits of the Famennean stage were investigated.

The distribution of the isotopic composition of carbon in the Devonian crudes areally is approximately the same as for the Tournaisian crudes. These crudes are similar in isotopic composition as well. An exception is represented by the Devonian crude oils of the Severo-kamskoye and Krasnokamskoye deposits, marked by a lighter isotopic composition. It should be noted that in the northern part of the Cis-Ural Trough (within the Solikamskaya depression), isotopically extremely light crude was encountered in the Famennean deposits (Durinskoye deposit -- $\delta C^{13} = -2{,}98$ percent).

Thus, there are definite correlations in the distribution of the isotopic composition of the carbon of the crudes investigated, areally. They are different somewhat for crudes relating to different productive complexes. In terms of isotopic composition of Middle Carboniferous and Visean crudes, conventionally a distinction is made between the northwest and southeast fields of the distribution with a well-defined boundary traceable along the southern margin of the Kamsko-Kinel'skoye system of troughs. This differentiation of isotopic composition has not been found for Devonian and Tournaisian crudes. But here a region within the Solikamskaya

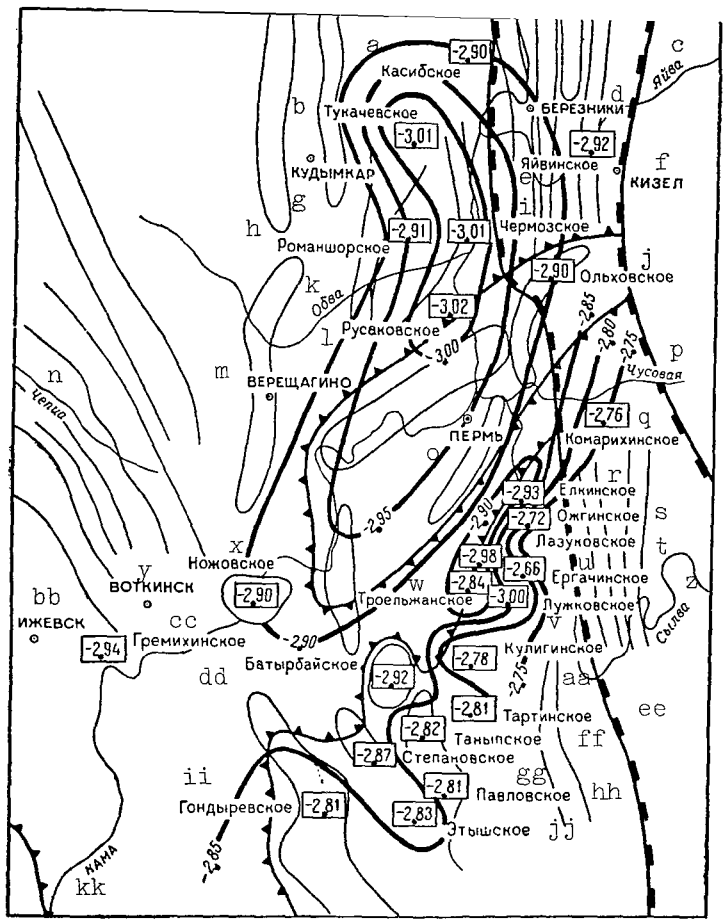

Fig. 34. Distributions of δC^{13} values (in percent) for crude oils from deposits of the Tul'sko-Bobrikovskiye deposits of the Visean of the Permian Ural Area. See Fig. 33 for symbols.

Key: a. Kasibskoye
b. Tukachevskoye
c. Yayva River
d. Berezniki
e. Yayvinskoye
f. Kizel
g. Kudymkar
h. Romanshorskoye
i. Chermozskoye
j. Ol'khovskoye
k. Obva River
l. Rusakovskoye
m. Vereshchagino
n. Cheptsa River
o. Perm'
p. Chusovaya River
q. Komarikhinskoye River
r. Yelkinskoye River
s. Ozhginskoye
t. Lazukovskoye
u. Yergachinskoye
v. Luzhkovskoye
w. Troyel'zhanskoye
x. Nozhovskoye
y. Votkinsk
z. Sylva River
aa. Kuliginskoye

[Key continued on following page]

[Key continued for Fig. 34 on preceding page]:

bb. Izhevsk	gg. Stepanvskoye
cc. Gremikhinskoye	hh. Pavlovskoye
dd. Batyrbayskoye	ii. Gondyrevskoye
ee. Tartinskoye	jj. Etyshskoye
ff. Tanypskoye	kk. Kama River

depression has been isolated where Tournaisian and Devonian crudes are enriched in the light isotope relative to the crudes of the same age from different regions.

Fig. 35 shows the distribution of the isotopic composition of carbon in crudes from deposits in different productive complexes. For the Middle Carboniferous and Visean deposits, an absolutely well-defined difference appears in crudes as to isotopic composition as a function of their territorial origin. The differentiation of isotopic composition based on this feature for Tournaisian and Devonian crudes is much less strongly pronounced, but the isotopically lightest samples of crudes pertain to deposits in the Solikamskaya depression.

The deposits of the southeast field over its entire profile contain isotopically heavy crudes, or the deposits of the Solikamskaya depression contain isotopically light crudes. Characteristic of the deposits in the northwest field is a more complicated distribution, enabling us to speak about the development here of crude oils of different genetical types. /153

The most ancient of the crudes investigated is the Upper Proterozoic crude. The carbon in this crude is enriched in C^{12} ($\delta C^{13} = -3{,}05$ percent). Petroleums of this isotopic composition are not encountered in the overlying profile. This enables us to state that crude oil from the Upper Proterozoic deposits did not migrate into the overlying deposits and the region of its distribution is limited to this complex.

Crude oils of the terrigenic Devonian are enriched in C^{13} ($\delta C^{13}_{av} = -2.81$ percent). To Tournaisian and Visean (Yasnopolyanskiye) crudes within the northwest field represent two different groups in isotopic carbon composition: Yasnopolyanskiye crudes ($\delta C^{13}_{av} = -2.94$ percent) are isotopically light, while Tournaisian crudes are among the isotopically heaviest ($\delta C^{13}_{av} = -2.76$ percent). Yasnopolyanskiye crudes represent a third genetical type of petroleum. As for the Tournaisian crudes, in isotopic composition they are virtually identical to the Devonian. True, an alternative remains open: are the Tournaisian crudes genetically a single whole common with the Devonian or do they represent a separate genetical type coincident in isotopic characteristic with the Devonian. The first variant, as shown by lithologo-facial analysis, is to be preferred. In any case, Tournaisian crudes within the northwest

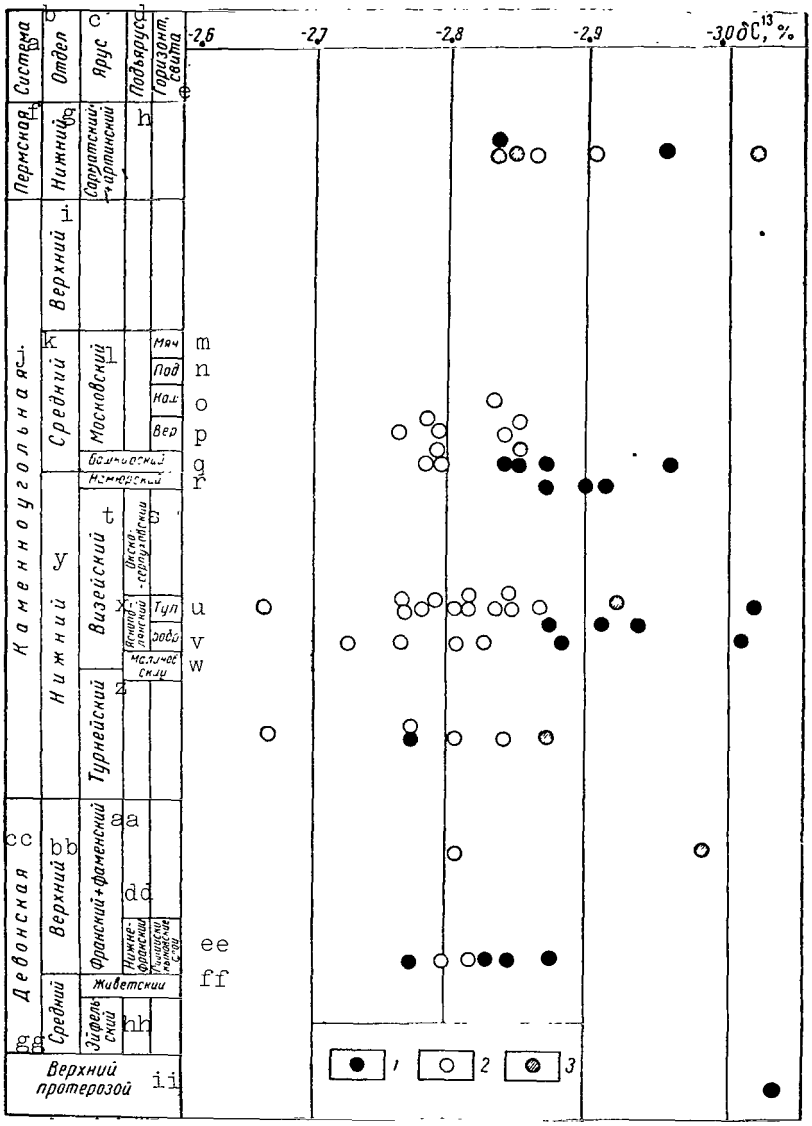

Fig. 35. Distribution of isotopic composition of crudes over the stratigraphic profile of the Permian Ural Area

1. northwest field
2. southeast field
3. Solikamskaya depression

Key: a. System
b. Series
c. Stage
d. Substage
e. Horizon, suite
f. Permian
g. Lower
h. Sarmatskiy + Artinskiy
i. Upper
j. Carboniferous
k. Middle
l. Moscovian
m. Myach.
n. Pod.

[Key continued on following page]

[Key continued for Fig. 35 on preceding page]:

o. Kash.
p. Ver.
q. Bashkirskiy
r. Namyurskiy
s. Oksko-Serpukhovskiy
t. Visean
u. Tul'skiy
v. Bobrinskiy
w. Malinovskiy
x. Yasnopolyanskiy
y. Lower
z. Tournaisian
aa. Franconian + Famennean
bb. Upper
cc. Devonian
dd. Lower Franconian
ee. Pashiysko-Kynovskiye strata
ff. Zhivetskiy
gg. Middle
hh. Eifelian
ii. Upper Proterozoic

field are not genetically associated with the Yasnopolyanskiye. In the literature on the geology of the Permian Kama Area, this fact is not taken note of. The prospects of the Lower Carboniferous deposits as regards petroleum are usually examined overall, without consideration of the fact that these prospects can differ for the Tournaisian and the Yasnopolyanskiye deposits owing to the difference in the genetical type of the crudes confined to them.

The values characterizing the limits of the variation in the isotopic composition of the carbon in the petroleum of the Middle Carboniferous and Permian deposits are close to the corresponding values for the carbon of the Yasnopolyanskiye crudes. In other words, by isotopic composition one cannot distinguish special genetical types corresponding to the crudes of the Middle Carboniferous and the Lower Permian. Results of analyzing the total carbon of these crudes do not contradict the possibility of their migration from Yasnopol skiye deposits, which incidentally, coincides with widely held view of geologists on this subject.

Since petroleum constituents have different isotopic composition of carbon, it can be assumed that the isotopic composition of petroleum carbon to a large extent is controlled by its constituent composition, in particular, by its group composition.

Fig. 36 compares the isotopic composition of the carbon of several crudes of the Permian Ural Area and their content of aromatic-fraction hydrocarbons. The coefficient of correlation is quite low. In exactly the same way, there is no relationship between the isotopic composition of carbon in crudes and their content of tars (Fig. 37) and sulfur (Fig. 38). There is no correlation between the isotopic composition of carbon in petroleum and its specific gravity (Fig. 39).

However, crudes of the northwest field relating to different genetical types by carbon isotopic composition also have different chemical composition.

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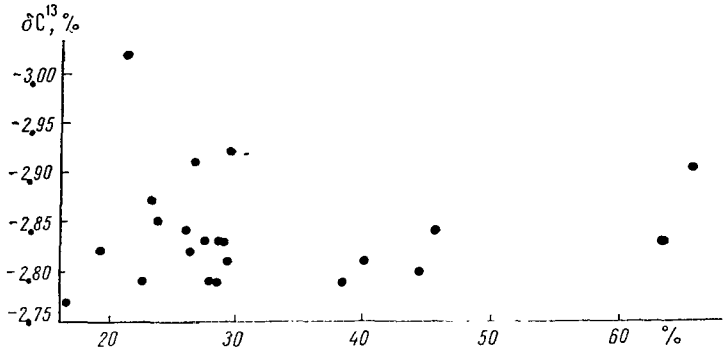

Fig. 36. Dependence of isotopic composition of carbon in petroleum (δC^{13}, percent) on its content of aromatic hydrocarbons (percent)

In Fig. 40, the concentrations of the methane, naphthenic, and aromatic hydrocarbons in different fractions are shown with triangle diagrams. As we can see, predominating in the gasoline fraction (60-200°C) are methane hydrocarbons, where the crudes of different productive horizons are not differentiated by the hydrocarbon composition of this fraction. In the higher-temperature fractions (200-550°C) there is marked differentiation of the content of hydrocarbon groups in the crudes of different productive horizons, where analyses of the hydrocarbon composition of crudes are groups in accordance with their origin to a particular stratigraphic horizon, which was seen even based on isotopic data.

This relationship however is not causal in nature. Both features from different aspects characterize the initial material of the given genetical type of petroleum. In other words, independently based on the isotopic and chemical (200-500°C fraction) compositions, a genetical difference is established between the /156
crudes of the isolated stratigraphic complexes. We note that the fraction of the higher-molecular petroleum hydrocarbons proves to be informative in the genetical respect.

When the ranges of variation in the isotopic composition of crudes from productive complexes of deposits in the southeast field were compared (see Fig. 35), no difference was detected, which could indicate their genetical dissimilarity.

Table 37 gives the results of an analysis of the isotopic composition of carbon in crudes over the profile of several multistratal deposits. Within the southeast fields, the isotopic composition of the carbon in crudes both over the profile of each deposit as well as within each stratigraphic complex of different deposits changes

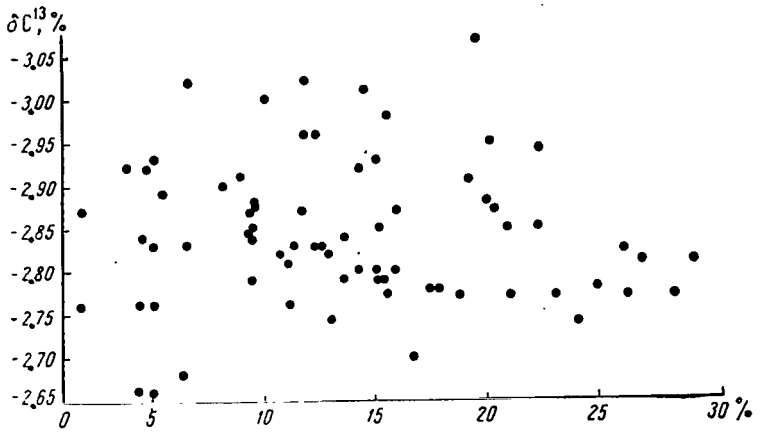

Fig. 37. Dependence of isotopic composition of carbon in crudes (δC^{13}, percent) of the Permian Ural Area on their tar content (percent)

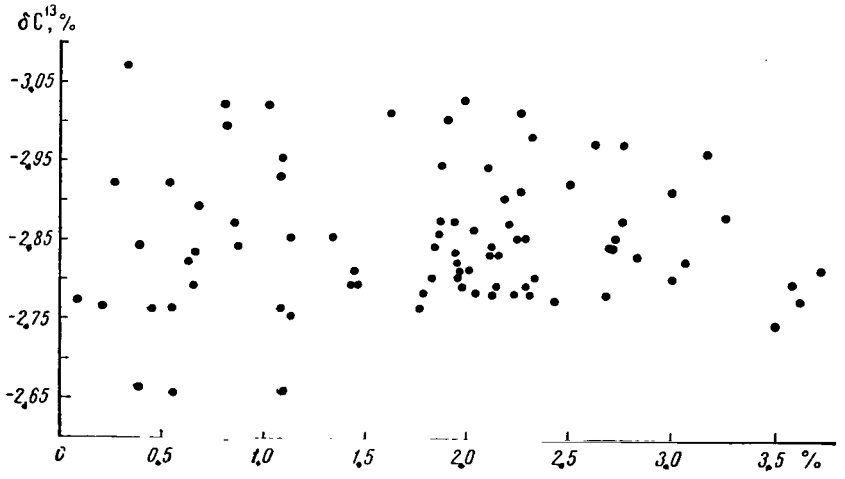

Fig. 38. Dependence of isotopic composition of carbon in crudes (C^{13}, percent) of the Permian Ural Area on their sulfur content (percent)

only slightly. The mean isotopic composition of Tournaisian crudes is -2.76 percent, Visean crudes -2.79 percent, and Middle Carboniferous -- -2.79 percent. All the crudes are isotopically heavy (the δC^{13} for the 18 Lower Carboniferous, Visean, and Tournaisian pools of deposits of the southeast field, given in Table 37, do not exceed the limits -2.84 percent).

TABLE 37. DISTRIBUTION OF ISOTOPIC COMPOSITION OF CARBON IN CRUDES (δC^{13}, PERCENT) IN PROFILES OF MULTISTRATAL DEPOSITS

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Stratigraphic complex	Deposits of southeast field				Nozhovskoye and Osinskoye deposits of northwest field
	Komarikhinskoye	Tanypskoye	Pavlovskoye	Gondyrevskoye	
P_1a	—2,86	—	—	—	—
C_2vr	—2,84	—2,79	—2,76	—	—
C_2b	—	—2,79	—2,79	—2,78	—2,90
C_1tl	—2,76	—2,83	—2,81	—2,84	—2,90
C_1bb	—2,77	—2,82	—2,80	—2,76	—2,88
C_1t	—2,66	—2,81	—2,80	—2,77	—2,77

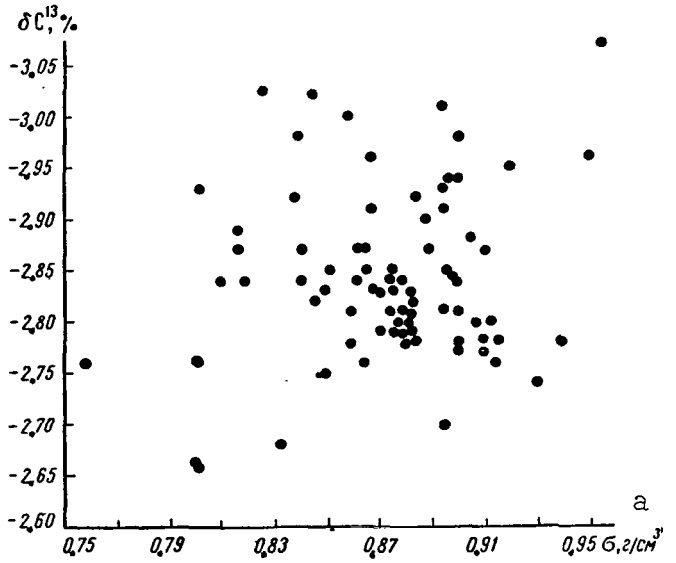

Fig. 39. Dependence of isotopic composition of carbon of crudes from the Permian Ural Area on specific gravity

Key: a. g/cm^3

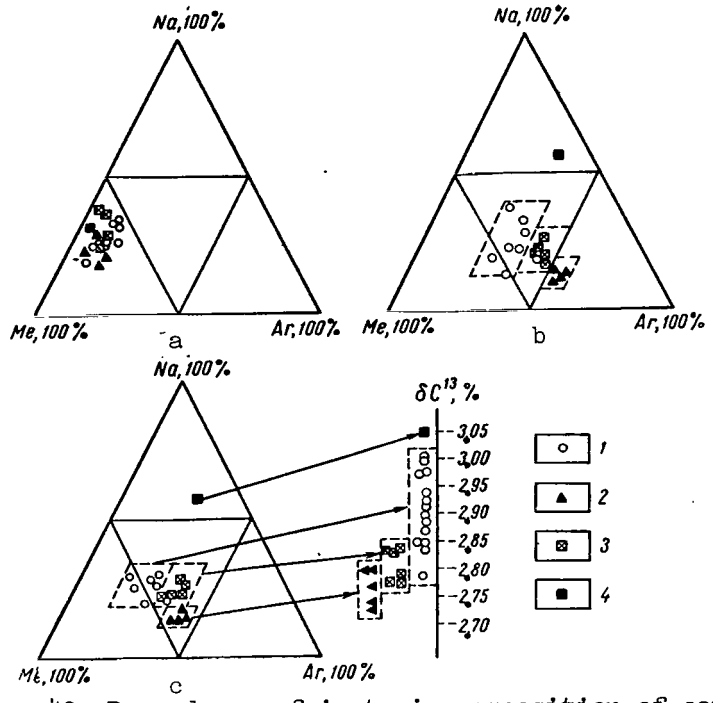

Fig. 40. Dependence of isotopic composition of carbon of crudes on group composition of fractions. a. 60-200° C b. 200-550° C c. 60-550° C. Productive horizons of Permian Ural Area: 1 - Visean 2 - Tournaisian 3 - Devonian 4 - Riphean

Thus, the distribution of the isotopes of carbon in crudes profilewise within the southeast field can be viewed as an argument in favor of the genetical commonality of the pools in different productive horizons. Quite remarkable in this respect is also the similarity of the distribution curves of the isotopic composition of the low-temperature fraction to aromatic hydrocarbons of the Tournaisian, Yasnopolyanskiye and Middle Carboniferous crudes of the Tanypskoye deposit (see Figs. 44-46). /158

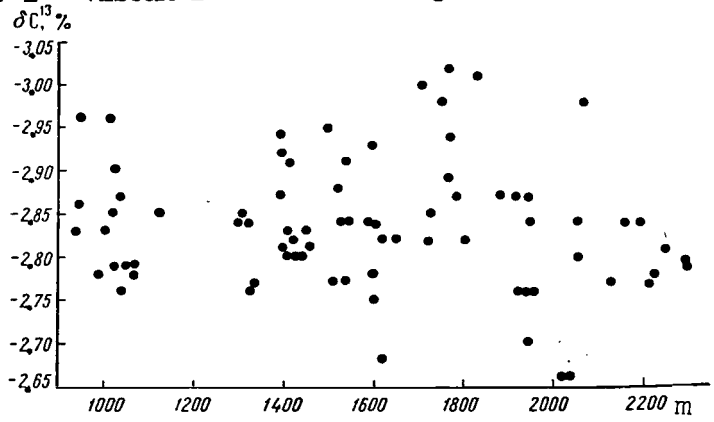

Fig. 41. Dependence of isotopic composition of carbon in crudes of the Permian Ural Area depth of bedding

Within the northwest field, multistratal deposits are virtually absent. Table 37 gives unified data for the Osinskoye (C_2b) and Nozhovskoye (C_1tl, C_1bb, C_1t) deposits. Here Tournaisian crudes as usual are heavier -- $\delta C^{13} = -2{,}77$ percent, but the Visean and the Lower Carboniferous are considerably enriched in the light isotope

(δC^{13}_{av} = -2.90 percent). With this example we have quite clearly manifested the genetical different classes of the Tournaisian crudes, on the one hand, and the Visean-Lower Carboniferous crudes -- on the other, established for deposits in the northwest field.

It should be noted that evidently, there is no correlation at all between the isotopic composition of crude and the lithological type of reservoir (see Table 36). Crudes lying in carbonate reservoirs (Tournaisian and Middle Carboniferous) have different isotopic composition; also differing in isotopic composition of the Devonian and Yasnopolnanskiye crudes lying in terrigenic reservoirs. When the isotopic composition of the carbon in crudes is compared with depth of bedding, no correlation is observed either (Fig. 41).

Thus, the factors that primarily control the isotopic composition of carbon in petroleum as a whole include its territorial confinement and its membership in a stratigraphic complex. In turn, /159 this means that the isotopic composition of petroleum carbon must reflect the characteristic existence of the establishment of the oil-gas bearing status of the given region.

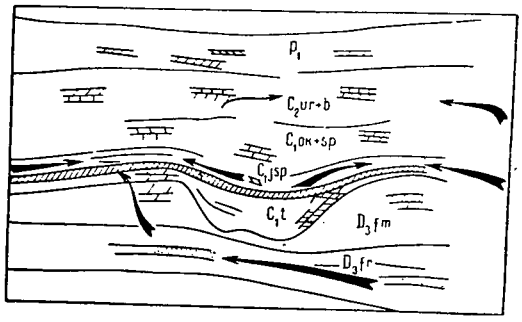

Fig. 42. Hypothesized scheme of migration of petroleum during formation of petroleum pools in the Permian Ural Area (conditional profile across the Kamsko-Kinel'skaya depression)

The forming of pools of petroleum and gas within an oblast, considering the foregoing concerning the role of the seismic factor, most obviously be related to the period in which the folded Urals was formed. Subsidence of the Kamsko-Kinel'skaya depression occurred much earlier (in post-Franconian time) [1], and its southwest margin delimits the regions of the distribution of the crudes of different isotopic composition. The Kamsko-Kinel'skaya depression stands out in the profile by the greatly increased thicknesses of the Fammenean deposits and the terrigeno-carbonate formations of the Saraylinskaya suite of the Tournaisian. Malinovskiye clays underlying the productive Tul'sko-Bobrikovskiye (Yasnopolyanskiye) deposits also have increased thicknesses within the Kamsko-Kinel'skaya depression. The formation of the depression was completed in the Oksko-Serpukhovskoye time. It is weakly manifested in the overlying deposits.

Thus, by the period of the most active phase of the Hercynian tectogenesis pertaining to Permian time, the Kamsko-Kinel'skaya

depression in the residual section has a profile that is near-Recent. As a result of seismic activity accompanying tectogenesis, processes of the migration and accumulation of hydrocarbons gained wide development, and in the southern part of the migratory region there was probably a general direction from southeast to northwest -- from the buried deposits of the Eastern Slope of the then-already formed Bashkirskiy Anticline and the Sylvenskaya depression.

It is not precluded that in the last case the pools formed through the simultaneous filling of traps over the entire profile due to a migratory flow whose source could have been some single type of subsided petroleum-producing deposit. Here the Kamsko-Kinel'skaya depression served as a barrier on the path of the migratory flow extending through the Tournaisian and Visean deposits (Fig. 42). However, it did not block the movement of petroleum in the same direction within the limits of the terrigenic Devonian. /160 Therefore, isotopically heavy crudes could have advanced northward and formed the oil pools in the deposits of the terrigenic Devonian and the hydrodynamically associated Tournaisian deposits within the northwest field.

The forming of pools occurred independently in the Yasnopolyanskiye deposits of the northwest field. Here the petroleum-producing deposits may have been the deposits of the Kamsko-Kinel'skaya depression (possibly, Malinovskiye clays). But the pools could have formed also through the filling of traps present in the zone directly adjoining the local trough or depression containing deposits capable of petroleum formation and petroleum release. As a result, the isotopically light crudes of this generation spread over the territory of the northwest part of the province, including the southern margin of the Kamsko-Kinel'skaya depression and the local structures within its limits. Along the southeast margin of the Kamsko-Kinel'skaya depression, within the bounds of the Yasnopolyanskiye deposits a boundary of the collision of two migratory pools of crudes of different generation apparently extends, therefore here at times isotopically heavy and isotopically light crudes could exist in nearby structures. This is particularly characteristic of the deposits in the zone of the Veslyanskiy and Mazuninskiy troughs complicated by dislocations (Yelkinskoye - $\delta C^{13} = -2.93$ percent; Ozhginskoye -- $\delta C^{13} = -2,72$ percent; Yergachinskoye -- $\delta C^{13} = -2,6$ percent; and Luzhkovskoye -- $\delta C^{13} = -3,00$ percent).

If one accepts that the presence of oil in the Lower Carboniferous deposits was due mainly to vertical migration from the terrigenic Visean, the corresponding tendency in the distribution of carbon isotopes areally must be manifested also in these deposits, but obviously in a less pronounced form, which we actually observed. Finally, the Solikamskaya depression possibly was controlled by one more type of the formation of crudes within the province, in which the oil content of the entire profile is associated with isotopically light crudes.

Chemistry of Isotopes of Petroleum Carbon

Distribution of Carbon Isotopes in Structural Groups of Petroleum Hydrocarbons

The distribution of carbon isotopes in hydrocarbons as a function of their structure and molecular weight reflects the most subtle aspects of the formation and transformation of crudes. The similarity of difference between crudes as to details of the distribution of carbon isotopes in the corresponding hydrocarbon constituents can serve as a convincing indicator of their genetical type origin or genetical difference. Therefore study of the isotopic composition of structural constituents and the low-temperature fractions of crudes is an essential part of the problem of our investigations.

The isotopic composition of carbon was separately analyzed in /161 normal paraffinic, isoparaffinic, and naphthenic hydrocarbons, and also in mono-, bi-, and polyaromatic hydrocarbons. The preparative procedure was carried out by A. Z. Koblova with a group of coworkers at the Kama Branch of the All-Union Scientific Research Geologo-Prospecting Petroleum Institute. Three temperature fractions of the crude oil were studied: 60-150°C, 150-300°C, and 300-500°C by thermo-vacuum distillation. The aromatic hydrocarbons were isolated by passing the corresponding fraction through a silica gel column. The adsorbed aromatic hydrocarbons were washed successively with different solvents; this yielded, separately, the light (Ar I), middle (Ar II), and heavy (Ar III) fractions of the aromatic hydrocarbons corresponding, approximately, to the monoaromatic, biaromatic, and aromatic higher degrees of cyclicity. The methane-naphthenic fraction liberated from the aromatic hydrocarbons was treated with carbamide in order to isolate the normal paraffins and the filtrate containing the isoparaffinic and naphthenic hydrocarbons was treated with thiocarbamide, capable of forming a complex with the isoparaffins. The hydrocarbons remaining in the filtrate were identified as naphthenic. The nature of the isolated products was monitored by their index of refraction.

It must be borne in mind that carbamide does not exhibit 100-percent selectivity with respect to normal hydrocarbons. Besides normal hydrocarbons, complexes with carbamide can be formed also by isoparaffinic hydrocarbons that have a normal chain containing at least eight carbon atoms at their end. Accordingly, the fraction of normal hydrocarbons can include isoparaffins, in particular, molecules that are 1-methyl substituted at the extreme carbon atoms. Thiocarbamide forms a complex with methyl-, dimethyl-, and more highly substituted paraffinic hydrocarbons, therefore the fraction isolated in the complex with thiocarbamide must be regarded not as an isoparaffinic, but more properly as a fraction of branched paraffinic hydrocarbons. But in several cases thiocarbamide does

TABLE 38. ISOTOPIC COMPOSITION OF CARBON IN STRUCTURAL GROUPS OF HYDROCARBONS IN FRACTIONS OF CRUDE OF THE UPPER DEVONIAN FROM PERMSKAYA OBLAST*

Temperature fraction °C	Yield for petroleum	Isotopic composition δC^{13}, %						
		Me+Na	n-Me	i-Me	Na	Ar I	Ar II	Ar III
60—150	12.8	—2.88	—	—	—	—2.84	—2.83	—
150—300	31.8	—2.92	—2.96	—	—	—2.92	—2.85	—
300—500	29.2	—2.95	—3.00	—	—2.86	—2.86	—2.96	—2.81

* Krasnokamskoye Deposit, square 207.

TABLE 39. ISOTOPIC COMPOSITION OF CARBON IN STRUCTURAL GROUPS OF HYDROCARBONS IN FRACTIONS OF UPPER CARBONIFEROUS CRUDE OILS OF PERMSKAYA OBLAST* /162

Temperature fraction, °C	Yield for petroleum	Isotopic composition δC^{13}, %						
		Me+Na	n-Me	i-Me	Na	Ar I	Ar II	Ar III
60—150	15.5	—2.88	—	—	—	—2.88	—2.81	—
150—300	30.2	—2.96	—3.05	—2.87	—2.93	—2.84	—2.86	—2.80
300—500	31.1	—2.90	—2.98	—2.80	—	—2.89	—2.78	—2.70

* Krasnokamskoye Deposit, square 21.

not form a complex with strongly branched isoparaffinic hydrocarbons containing alkyl (for example, butyl) radicals as substituents. The latter, therefore, with the precedure adopted fall in the naphthenic fraction. The results of analysis are given in Tables 38 and 39.

Paraffinic-naphthenic hydrocarbons overall are isotopically lighter than aromatic, and the difference in the isotopic composition is less noticeable in the low-boiling fraction and increases in the high-boiling fraction.

A more detailed study of the paraffinic-naphthenic and aromatic fractions shows that here there is a characteristic distribution of the carbon isotopes in different structural groups. The isotopically lightest component of the paraffinic-naphthenic fraction proved to be the normal hydrocarbons. Isoparaffinic hydrocarbons are noticeably enriched in the heavy isotope. In the kerosene and oil fractions of Middle Carboniferous petroleum, the shift toward the side of enrichment in the heavy isotope in both cases is identical (0.18 percent).

In isotopic composition, naphthenic hydrocarbons occupy an intermediate position in the (n = Me + i = Me + Na)-fraction. A distinct trend toward enrichment of the higher cyclic compounds in the heavy carbon isotope is observed in the aromatic fraction.

Distribution of Carbon Isotopes in Narrow Temperature Fractions of Paraffinic-Naphthenic and Aromatic Hydrocarbons of Petroleum /163

Initially, the total carbon in fractions was studied without separation into methane-naphthenic and aromatic constituents, which in view of the established difference in the isotopic composition of carbon in different structural groups appears not entirely specific.

S. Silverman [219] analyzed low-temperature fractions in one petroleum sample from California. With the mean isotopic composition of petroleum of -2.24 percent , methane has $\delta C^{13} = -3{,}80$ percent. From methane to hexane, the carbon successively is depleted in the light isotope and is characterized by δC^{13} from -2.7 to -2.26 percent. At temperatures above 100°C, the low-temperature fractions are somewhat depleted in C^{12} compared to the average for the petroleum; in the higher boiling fractions, beginning at 200°C, carbon again is somewhat enriched in the light isotope. S. Silverman believes that since the boiling point of hydrocarbons depends on their molecular weight, this distribution of carbon isotopes in the temperature fractions indicates the formation of both low-molecular hydrocarbons as well as hydrocarbons of moderate molecular weight from initial high-molecular and high-boiling compounds. Hydrocarbons with intermediate molecular weight were formed as a residual product (and therefore depleted in C^{12}) of the cleavage of low-molecular, isotopically light compounds from high-molecular petroleum hydrocarbons.

It should be noted that the distribution of carbon isotopes in low-temperature fractions of the crude oils we investigated from Permian Ural Area is more complicated in character and overall does not have the tendency noted by S. Silverman. P. Muller and R. Wienholz [198] studied petroleum fractions boiling to 100°C ($\delta C^{13} = -2{,}91$ percent), in the 100-150°C interval ($\delta C^{13} = -2{,}86$ percent), 150-200°C interval (δC^{13} = -2.88 percent), and above 200°C (δC^{13} = -3.08 percent) and found the successive enrichment of the higher boiling fractions in the light isotope for a mean δC^{13} of petroleum as a whole of -3.02 percent.

Data of S. Silverman, who gave the results of analyses of isotopic composition with respect to the zone working standard, have been recalculated by us to the PDB standard.

We studied the isotopic composition of total carbon in various temperature fractions of crude oils from deposits of different ages (pertaining to different stratigraphic complexes). As follows from Fig. 43, the nature of the distribution of carbon isotopes by fractions is quite close. In all cases, a relative enrichment in C^{13} was established for the lowest-boiling petroleum hydrocarbons: 60-95 and 95-122°C. In the last fractions, the isotope distribution in total carbon is more uniform. /164

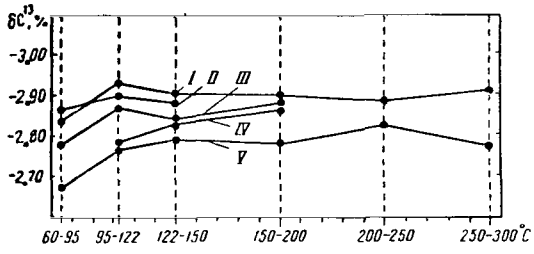

Fig. 43. Dependence of isotopic composition of total carbon on boiling point of petroleum fractions
I, II, III, IV, V. Vsevolodovil'venskoye (P_1s), Kuz'minskoye (C_1jsp), Ol'khovskye (C_1jsp), Nozhovskoye (C_1^t), and Bel'skoye (C_2b) deposits

The isotopic composition of the paraffinic-naphthenic portion and the total carbon in the fraction (Table 40) was compared in the gasoline fractions of crude oils from the Ol'khovskoye, Nozhovskoye, and Kuz'minskoye deposits. The carbon in the total fraction (containing the aromatic constituent) is isotopically heavier than the carbon of the paraffinic-naphthenic fractions. From the data given it also follows that enrichment of the 60-95°C fraction in the heavy isotope is associated not with the aromatic or naphthenic hydrocarbons, but with the isotopically heavy paraffinic hydrocarbons. Characteristic in this respect is the petroleum of the Kuz'minskoye Deposit, where the 60-95°C fraction as a rule is enriched in the heavy carbon isotope, in spite of the fact that this fraction is 96 percent methane hydrocarbons.

It was of interest to analyze Upper Proterozoic (Wendian) petroleum of the Sivinskoye Deposit containing only high-boiling fractions. This petroleum, the most ancient of those studied, is characterized by all the fractions being considerably enriched in the light carbon isotope (Table 41). The 300-350 and 350-400°C oil fractions were found to be enriched in the light isotope relative to the higher-boiling fractions. Also substantial was the amplitude in the fluctuations of the isotopic composition of carbon between adjoining fractions, here exceeding 0.1 percent. In the other crudes, the difference in the isotopic composition of the neighboring fractions rarely exceeds limits 0.05 percent.

Crudes from the Tanypskoye and Krasnokamskoye deposits underwent more detailed analysis; in their profile there were pools belonging to all the main productive horizons of the province. Features of similarity or difference in the isotope distribution

TABLE 41. CHARACTERISTICS OF UPPER PROTEROZOIC PETROLEUM* /165

Fractions, °C	Petr. yield %	Density, g/cm³,	Molec. wt.	Sulfur %	Group comp. of hydrocarbons, %			δC^{13}, %
					Ar	Na	Me	
Petroleum overall	—	0.9550	—	0.33	11.22	38.39	50.39	—3.05
300—350	14.97	0.8857	233	0.16	32.0	58.1	9.09	—3.12
350—400	6.93	0.9255	305	0.21	35.71	57.22	7.07	—3.19
400—450	13.36	0.9427	359	0.23	38.38	45.90	15.72	—3.02
450—500	7.50	0.9523	382	0.25	31.08	57.90	11.02	—3.09
500—550	7.35	0.9621	491	0.30	28.55	70.02	1.47	—3.12
Solid paraffin	0.95	—	—	—	—	—	—	—
Tars	19.62	—	—	—	—	—	—	—3.04
Asphaltenes	8.95	—	—	—	—	—	—	—3.02

* Sivinskoye deposit, square 1, sampling interval 2788-2800 m

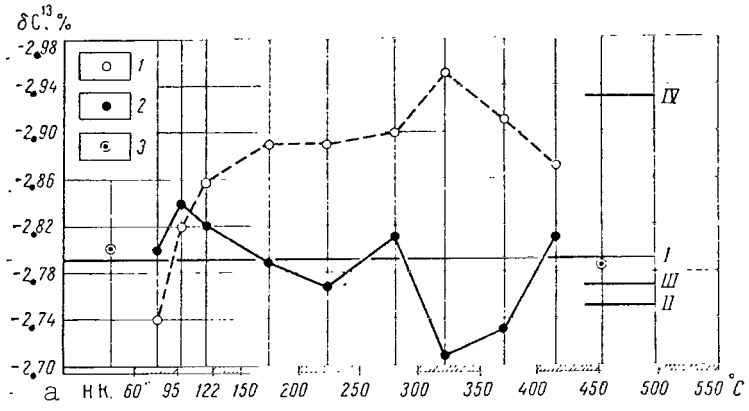

Fig. 44. Dependence of isotopic composition of carbon in Middle Carboniferous (C_2b) crudes from the Tanypskoye Deposit (square 64) on the boiling point of fractions
1. Me + Na-fraction
2. Ar-fraction
3. total carbon of fractions
I-IV. isotopic carbon of petroleum overall, tars, asphaltenes, and paraffin
KEY: a. Beginning of boiling

TABLE 40. CHARACTERISTICS OF CARBON IN GASOLINE FRACTIONS OF CRUDE OILS

Deposit, bore hole number	Stratigr. complex	Interval m	Fraction °C	Group composition of carbons %				δC^{13}, ‰
				Me	Na	Ar	Me+Na	Me+Na+Ar
Ol'khovskoye 17	C_1jsp	1838—1843	60—95	65.30	32.16	2.53	—2.82	—2.78
			95—122	60.81	28.63	10.56	—2.95	—2.87
			122—150	52.67	32.97	14.36	—2.93	—2.84
			150—175	58.41	20.57	21.02	—2.97	—2.88
Nozhovskoye 6	C_1t	1521—1552	60—95	81.93	17.38	0.69	—2.74	—
			95—122	74.80	23.30	1.92	—	—2.78
			122—150	57.20	38.76	3.02	—2.93	—2.86
			150—187	50.97	40.04	8.99	—2.90	—2.89
Kuzminskoye 85	C_1jsp	1720—1740	60—95	95.95	2.21	1.84	—2.85	—2.86
			95—122	75.41	18.23	6.36	—2.91	—2.89
			122—150	65.76	20.76	13.48	—2.91	—2.87

and the low-temperature fractions and constituents of the crudes understandably can more convincingly pool their genetical common origin than the results of comparing the isotopic composition only of total carbon. The isotopic composition of fractions of crude oils from the three productive complexes of Tanypskoye Deposit (Tournaisian, Visean, and Middle Carboniferous) located within the Permsko-Bashkirskiy Anticline south of the Kamsko-Kinel'skaya system of troughs was analyzed, as well as Devonian petroleum and Bashkirskaya petroleum from Krasnokamskoye Deposit located in the /166
northern part of the Permsko-Bashkirskiy Anticline on the other side of the Kamsko-Bashkirskaya Depression.

As can be seen from Figs. 44-48, among the crude oils belonging to different stratigraphic complexes, there are none whose distribution curves of isotopic composition by fractions would be conformable in all respects. However, noteworthy is the similarity in the distribution curves of the carbon isotopes in the aromatic constituent of the temperature fractions of crudes from all the three pools analyzed from the Tanypskoye Deposit (Figs. 44-46). This similarity is further underscored by the different nature of the distribution of carbon isotopes in aromatic hydrocarbons of Devonian petroleum of the Krasnokamskoye Deposit (Figs. 47 and 48). But there is no noticeable parallelism in the distribution of carbon isotopes in the methane-naphthenic constituent of the temperature fractions of these same crudes. Moreover, the distribution curve for the methane-naphthenic fractions of Tournaisian Crude of the Tanypskoye Deposit is much closer to the corresponding curve for the Devonian crude from the Krasnokamskoye Deposit than for the overlying crudes of the same Tanypskoye Deposit.

Evidently, analyses are needed for series of crudes from the same horizon and the same pool before one can judge the extent to which the distribution of carbon isotopes in the fractions of the corresponding petroleum is characteristic for the given horizon (pool). /167

At the same time, there are common to all crudes correlations that obviously reflect general correlations in the formation of the hydrocarbon composition of the petroleum. In all crudes the methane-naphthenic hydrocarbons as a whole (from the sum of all fractions) are enriched in C^{12} relative to the aromatic hydrocarbons. The isotopic composition of the methane-naphthenic hydrocarbons varies with increase in molecular weight (boiling point) toward the side of enrichment in C^{12}. In all the crudes the methane-naphthenic constituent of the 60-95 and 95-122°C fractions is considerably depleted in the light isotope. In the higher boiling fractions the differentiation is less noticeable. The isotopic composition of solid paraffin is close to the mean isotopic composition of the methane-naphthenic fractions boiling at temperatures from 250 to 450°C.

As a possible explanation of the singular enrichment in C^{13} of the low-boiling fractions of crudes (60-95 and 95-122°C), we could suggest that this phenomenon was caused by the partial loss of light fractions by the crudes. Here the evaporation was accompanied by an isotopic effect (enrichment of the isotope in the gaseous phase in the light isotope compared with the same hydrocarbon in the liquid phase), the fraction remaining in the crudes should have been enriched in the heavy isotope. In order to verify this assumption, experiments were conducted studying the isotope effect of Rayleigh dispersion of individual hydrocarbons, including n-hexane that is present in the 60-95°C fraction. It was established that evaporation of the hydrocarbons analyzed was not accompanied by a measurable isotope effect. Thus, the assumption that enrichment of the low-boiling methane-naphthenic hydrocarbons in the light isotope results from the loss by the crude of part of the low-boiling hydrocarbons was not experimentally confirmed and can be stricken from consideration.

Isoparaffin hydrocarbons present in the methane-naphthenic fraction are marked by heavier isotopic composition, therefore the enrichment in C^{13} of the methane-naphthenic constituent of low-boiling fractions characteristic of the crudes analyzed can be accounted for by the increased content in these fractions of paraffinic hydrocarbons of iso-structure. As we know, in crudes isoparaffinic hydrocarbons are usually actually concentrated in the low-temperature fractions. However, unfortunately in this case we do not have materials on the content of isoparaffinic hydrocarbons in the fractions of the crudes analyzed.

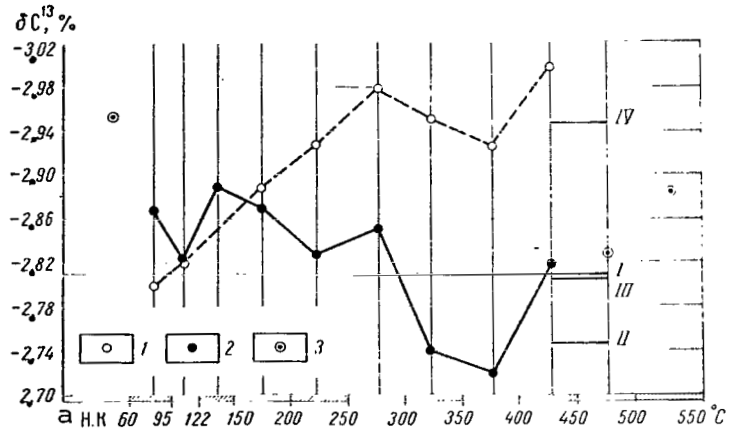

Fig. 45. Dependence of isotopic composition of carbon in Yasnopolyanskiye (C_1t1) crudes of the Tanypskoye Deposit (square 21) on the temperature boiling interval of fractions

1. Me + Na-fraction
2. Ar-fraction
3. total carbon in fraction

I-IV. isotopic composition of petroleum as a whole, tars, asphaltene, and paraffin

Key: a. beginning of boiling

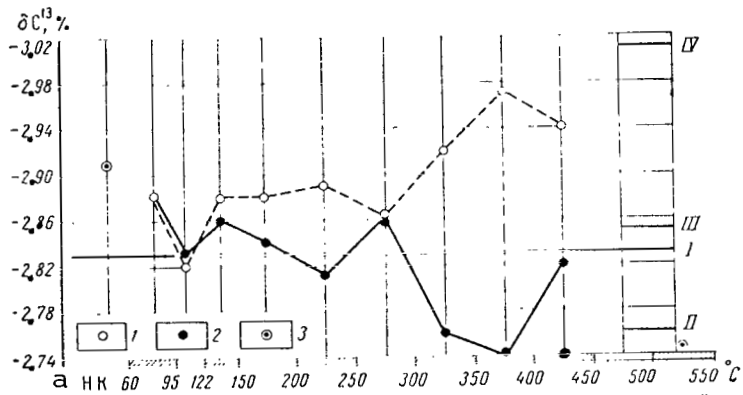

Fig. 46. Dependence of isotopic composition of carbon in Tournaisian crudes (C_1t) of Tanypskoye Deposit (square 103) on boiling temperature interval of fractions

1. Me + Na-fraction
2. Ar-fraction
3. total carbon of fractions

I-IV. isotopic composition of petroleum as a whole, tars, asphaltene, and paraffin

Key: a. beginning of boiling

In contrast to the methane-naphthenic fraction, aromatic hydrocarbons are enriched in the heavy isotope with increase /169 in molecular weight. Thus, a relative constancy of the isotopic composition of carbon in the total fractions of crudes that has been noted resulted from superpositioning two oppositely oriented tendencies -- enrichment of the methane-naphthenic fraction in the light isotope and enrichment of the aromatic fraction in the heavy isotope, with increase in the boiling point of the fraction. The latter entirely finds a simple explanation, since an increase in /168 cyclicity must lead to concentration of C^{13}.

An increase in the molecular weight of aromatic hydrocarbons occurs through an increase not only in the number of aromatic rings, but also in the number in length of the chain of side alkyl substituent so by the addition to the aromatic ring of a naphthenic ring. As was shown above, the isotopic composition of aromatic hydrocarbons depends on the structural type.

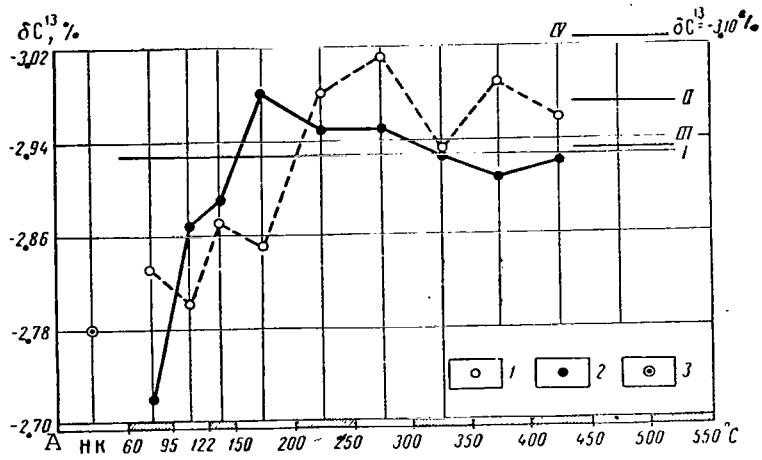

Fig. 47. Dependence of isotopic composition of carbon in Middle Carboniferous (C_2b + vr) crudes from the Krasnokamskoye Deposit (square 21) on the temperature boiling interval of fractions

1. Me + Na-fraction
2. Ar-fraction
3. total carbon of fractions

I-IV. isotopic composition of petroleum as a whole, tars, asphaltene, and paraffin

Key: A. Beginning of boiling

The predominance in the narrow-temperature fraction of an aromatic hydrocarbon of any single structural type can cause a marked deviation in the isotopic composition of the corresponding fraction from some averaged curve reflecting a general tendency to enrichment of higher boiling fractions in the heavy carbon isotope. Thus, in all crudes analyzed noteworthy for the relatively isotopic composition compared with the neighboring fractions is the aromatic fraction boiling at 250-300°C. It is precisely at temperatures of 250-300°C (Tables 42-46) that there is a sharp drop in the content of naphthenic hydrocarbons and increase in the content of methanic hydrocarbons compared with the adjoining fractions (in Tables 42-46 data pertaining to the 250-300°C fraction has been singled out). And for the aromatic constituent the smooth rise in its relative content with increase in boiling point here is not disrupted at all.

Probably, the relative enrichment of the aromatic constituent of the 250-300°C fraction in C^{12} can be associated with this feature of the group composition of this fraction, by assuming that aromatic hydrocarbons boiling at 250-300°C are represented chiefly by monocyclic compounds with several aliphatic substituents, while in the neighboring fractions the hydrocarbons are bicyclic, and in the

200-250°C fraction these are more generally hydrocarbons with a single aromatic and single naphthenic ring, while in the 300-350°C fraction -- with two or more aromatic rings. This explanation correlates with the results of the analysis of aromatic hydrocarbons of different structural types (see Tables 38 and 39).

By analyzing the isotopic composition of temperature fractions, it was found that aromatic hydrocarbons in the lowest-boiling fractions (60-95 and 95-120°C) are isotopically lighter than the methane hydrocarbons. This inversion in the ratios of isotopes in the aromatic and methane-naphthenic constituents comes from two oppositely oriented tendencies: on the one hand, depletion in the light carbon isotope of the methane hydrocarbons with decrease in their molecular weight, and on the other hand, an increase in the content of the heavy isotope in aromatic hydrocarbons as their molecular weight is increased.

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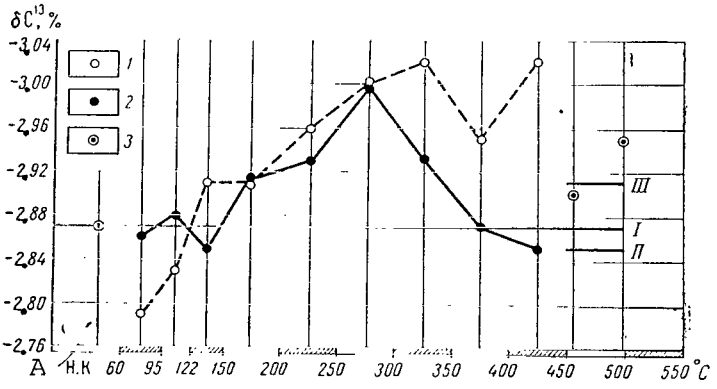

Fig. 48. Dependence of isotopic composition of carbon in Devonian (D_3) crudes from the Krasnokamskoye Deposit (square 207) on the temperature boiling interval of fractions
1. Me + Na-fraction
2. Ar-fraction
3. total carbon of fractions
I-III. isotopic composition of petroleum as a whole, tars, and asphaltene
Key: A. Beginning of boiling

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TABLE 42. ISOTOPIC COMPOSITION OF PETROLEUM FRACTIONS FROM THE KRASNOKAMSKOYE DEPOSIT (SQUARE 21, HORIZON C_2b+vr; SAMPLING INTERVAL 1120-1128 m)

Temperature interval of fractions °C	Petr. yield %	Density, g/cm³	Molec. wt.	Sulfur %	Group comp. of hydrocarbons, %			δC¹³, %	
					Ar	Na	Me	Me+Na	Ar
Petrol. overall	—	0.8493	—	1.08	20.58	21.43	57.99	−2.93	
Beginning of boiling −60	1.26	0.6508	—	—	—	—	—	−2.78	
60—95	3.57	0.6729	80.9	—	6.44	19.65	73.91	−2.83	−2.72
95—122	3.43	0.7173	96.7	—	6.72	26.47	66.81	−2.80	−2.87
122—150	5.24	0.7422	109.2	—	9.07	41.83	49.10	−2.87	−2.80
150—200	8.96	0.7699	133.3	—	15.00	36.55	48.45	−2.85	−2.98
200—250	10.46	0.8082	165.7	—	17.14	39.77	43.69	−2.98	−2.95
250—300	10.99	0.8338	171.8	—	24.29	18.93	56.78	−3.01	−2.95
300—350	8.96	0.8636	—	0.91	23.8	35.7	41.3	−2.93	−2.93
350—400	8.61	0.8860	—	1.11	34.2	25.3	40.5	−2.99	−2.91
400—450	7.47	0.9099	—	1.27	38.6	17.2	44.2	−2.96	−2.92
450—500	7.53	0.9273	—	1.47	44.1	6.43	49.5	−2.90	
500—550	5.30	0.9373	—	1.69	50.3	7.46	42.25	−2.89	
Solid paraffin	4.44	—	—	—	—	—	—	−3.10	
Tars	7.04	—	—	—	—	—	—	−2.97	
Asphaltenes	1.74	—	—	—	—	—	—	−2.93	

TABLE 43. ISOTOPIC COMPOSITION OF NARROW-TEMPERATURE PETROLEUM FRACTIONS FROM THE TANYPSKOYE DEPOSIT (SQUARE 21, HORIZON $C_1t\ell$, SAMPLING INTERVAL 1408-1412 m)

Temperature interval of fractions, °C	Petr. yield %	Density, g/cm³	Molec. wt.	Sulfur %	Group cont. of hydrocarbons			δC¹³, %	
					Ar	Na	Me	Me+Na	Ar
Petrol. overall	—	0.8749	—	1.84	28.94	13.29	57.77	−2.83	
Beginning of boiling −60	1.79	—	—	—	—	—	—	−2.91	
60—95	7.83	0.6905	95	0.15	4.76	15.71	79.53	−2.88	−2.88
95—122	2.83	0.7392	114	0.41	9.00	17.12	73.88	−2.82	−2.83
122—150	0.93	0.7500	116	0.50	10.71	29.02	60.27	−2.88	−2.86
150—200	5.65	0.7716	134	0.87	16.05	34.42	49.53	−2.88	−2.84
200—250	8.50	0.8065	159	1.40	25.11	33.32	41.57	−2.89	−2.81
250—300	13.64	0.8454	197	2.08	35.24	16.84	47.92	−2.86	−2.86
300—350	10.31	0.8917	—	2.20	48.1	17.90	44.0	−2.92	−2.76
350—400	6.58	0.9143	—	2.36	48.06	14.50	57.40	−2.97	−2.74
400—450	6.82	0.9310	—	2.36	54.6	7.90	57.42	−2.94	−2.82
450—500	6.80	0.9478	—	2.51	60.24	0.59	39.20	—	
500—550	6.73	0.9631	—	2.92	63.37	6.59	30.04	−2.74	
Solid paraffin	3.10	—	—	—	—	—	—	−3.01	
Tars	12.32	—	—	—	—	—	—	−2.76	
Asphaltenes	4.15	—	—	—	—	—	—	−2.85	

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TABLE 44. ISOTOPIC COMPOSITION OF NARROW-TEMPERATURE FRACTIONS OF PETROLEUM FROM THE TANYPSKOYE DEPOSIT (SQUARE 64, HORIZON C_2^b, SAMPLING INTERVAL 1044-1058 m)

Temperature interval of fractions, °C	Petr. yield %	Density, g/cm³	Molec wt.	Sulfur %	Group comp. of hydrocarbons %			δC¹³, %	
					Ar	Na	Me	Me+Na	Ar
Petroleum overall	—	0.8568	—	1.99	28.06	13.03	58.91	−2.79	
Beg. of boiling—60	1.06	—	—	—	—	—	—	−2.80	
60—95	7.61	0.6936	97	0.13	5.52	18.66	75.82	−2.74	−2.80
95—122	0.91	0.7344	108	—	9.96	20.80	69.24	−2.82	−2.84
122—150	1.70	0.7653	111	0.37	11.72	34.87	53.41	−2.86	−2.82
150—200	7.69	0.7697	129	0.43	18.94	33.69	47.42	−2.89	−2.79
200—250	9.52	0.8073	162	0.63	26.24	30.24	43.52	−2.89	−2.77
250—300	11.66	0.8438	202	1.37	24.27	14.46	51.27	−2.90	−2.81
300—350	10.95	0.8853	245	2.25	46.2	17.21	36.59	−2.95	−2.71
350—400	7.32	0.9072	313	2.33	48.96	6.63	44.41	−2.91	−2.73
400—450	7.52	0.9245	336	2.49	51.34	7.78	40.88	−2.87	−2.81
450—500	6.90	0.9422	448	2.59	55.73	2.21	42.06	−2.78	
500—550	5.00	0.9552	495	2.79	61.33	5.99	32.68	−2.77	
Solid paraffin	4.21	—	—	—	—	—	—	−2.93	
Tars	9.55	—	—	—	—	—	—	−2.75	
Asphaltenes	3.06	—	—	—	—	—	—	−2.78	

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TABLE 45. ISOTOPIC COMPOSITION OF NARROW PETROLEUM FRACTIONS FROM THE KRASNOKAMSKOYE DEPOSIT (SQUARE 207, HORIZON D_3, SAMPLING INTERVAL 1725.5-1728 m)

Temperature interval of fractions, °C	Petr. yield %	Density, g/cm³	Molec wt.	Sulfur S, %	Group comp. of hydrocarbons %			δC¹³, %	
					Ar	Na	Me	Me+Na	Ar
Petroleum overall	—	0.8455		0.67	19.17	19.21	61.62	−2.87	
Beginning of boiling—60	2.03	—	—	—	—	—	—	−2.87	
60—95	4.23	0.6743	87	0.3	9.08	17.05	73.87	−2.79	−2.86
95—122	4.12	0.7191	104	0.39	10.08	24.63	65.29	−2.83	−2.88
122—150	4.67	0.7425	112	0.5	9.45	38.03	52.52	−2.91	−2.85
150—200	9.14	0.7679	128	0.69	11.63	38.88	49.49	−2.91	−2.91
200—250	11.15	0.8022	164	0.70	16.80	33.28	49.92	−2.96	−2.93
250—300	8.55	0.8292	192	1.40	21.20	22.48	56.40	−3.00	−3.00
300—350	10.51	0.8565	237	0.48	30.52	29.53	39.95	−3.02	−2.93
350—400	8.71	0.8837	299	0.84	29.70	21.09	49.21	−2.95	−2.87
400—450	5.77	0.9009	330	0.97	34.44	11.80	53.76	−3.02	−2.85
450—500	7.68	0.9182	447	0.98	38.98	3.05	57.96	−2.90	
500—550	4.62	0.9323	489	1.19	47.90	—	52.10	−2.95	
Solid paraffin	5.83	—	—	—	—	—	—	—	
Tars	8.42	—	—	—	—	—	—	−2.85	
Asphaltenes	2.84	—	—	—	—	—	—	−2.91	

TABLE 46. ISOTOPIC COMPOSITION OF NARROW-TEMPERATURE FRACTIONS OF PETROLEUM FROM THE TANYPSKOYE DEPOSIT (SQUARE 103, HORIZON C_1t, SAMPLING INTERVAL 1457-1468 m)

Temperature interval of fractions °C	Petr. yield %	Density, g/cm³	Molec. wt.	Sulfur %	Group comp. of hydrocarbons %			δC¹³, %	
					Ar	Na	Me	Me+Na	Ar
Petroleum overall	—	0.8809	—	2.1	29.31	13.74	56.95	−2.81	
Beg. of boiling−60	1.33	—	—	—	—	—	—	−2.95	
60—95	3.79	0.6651	—	—	4.25	14.85	80.91	−2.80	−2.87
95—122	2.22	0.7038	—	—	5.16	20.97	73.87	−2.82	−2.82
122—150	3.52	0.7312	—	—	7.56	36.98	55.47	—	−2.89
150—200	7.32	0.7665	—	—	14.85	37.47	47.68	−2.89	−2.87
200—250	8.23	0.8240	—	—	24.77	33.10	42.13	−2.93	−2.83
250—300	13.51	0.8470	—	—	34.57	17.01	48.42	−2.98	−2.85
300—350	9.27	0.8910	—	2.56	48.05	18.44	33.51	−2.95	−2.74
350—400	6.95	0.9135	—	2.63	45.68	22.27	32.05	−2.92	−2.72
400—450	7.63	0.9298	—	2.70	56.46	5.01	38.53	−2.99	−2.82
450—500	6.76	0.9471	—	2.58	59.25	2.85	37.90	−2.83	
500—550	7.48	0.9583	—	2.82	65.60	2.58	51.82	−2.89	
Solid paraffin	2.98	—	—	—	—	—	—	−2.95	
Tars	29.38	—	—	—	—	—	—	−2.75	
Asphaltenes	2.30	—	—	—	—	—	—	−2.81	

Thus, the rule that aromatic hydrocarbons are isotopically heavier than methane-naphthenic is not absolute. It is fully valid only for high-boiling fractions for which the difference in the isotopic composition of the methane-naphthenic and aromatic hydrocarbons is 0.2 percent and more toward the side of increased content of the heavy isotope in the latter. Since, as follows from the value of the thermodynamic isotopic factors and direct analyses of the isotopic composition of aliphatic and aromatic structures of organic matter, aromatic compounds must be enriched in the heavy /175
isotope, the observed ratios of isotopes in the petroleum hydrocarbons show that the low-molecular hydrocarbons of petroleum must stand further removed genetically from the initial organic material than the higher-molecular hydrocarbons.

Experimental Study of Interphase Fractionation of Carbon Isotopes in Individual Hydrocarbons

It should at once emphasize that we are not talking about the separation of carbon isotopes between gaseous (low-molecular) and liquid (high-molecular) hydrocarbons in the oil-gas mixture. The isotope effects of this kind will be examined in the next chapter. The separation of isotopes was investigated between the part of the individual hydrocarbon compound in the liquid phase and the part of the compound in the gaseous (vapor) phase.

If the oil-gas pool forms a two-phase system, part of the liquid hydrocarbon can be in the gaseous phase as a vapor. If it is further assumed that the isotopic composition of the liquid hydrocarbon and that of its vapor differ, that is, there is a corresponding isotope effect, during "evaporation" of the oil pool the isotopic composition of the individual hydrocarbons present in the petroleum will change. This in turn can be reflected in the nature of the distribution curves of the carbon isotopes in /176
the temperature fractions.

Accordingly, to verify one of the possible explanations accounting for the specifics of the distribution of carbon isotopes in the temperature fractions of crudes, experiments were conducted to observe the isotope effects in the liquid-vapor system of several individual hydrocarbons.

The test hydrocarbon during the experiment was evaporated in volume 2 (Fig. 49). By means of ground-glass joints 3 and 6, vessel 2 can be shifted into two mutually perpendicular planes. This permits shifting the liquid during evaporation by evacuating vessel 2 and also converting vessel 2 into the vertical position and which the volume of the evaporating liquid is measured with respect to the level occupied by its residue in the calibrated arm 1. The spherical trap 7 fills with liquid nitrogen serves to condense the vapor. In trap 10 the streaming residue cooled by liquid nitrogen solidifies.

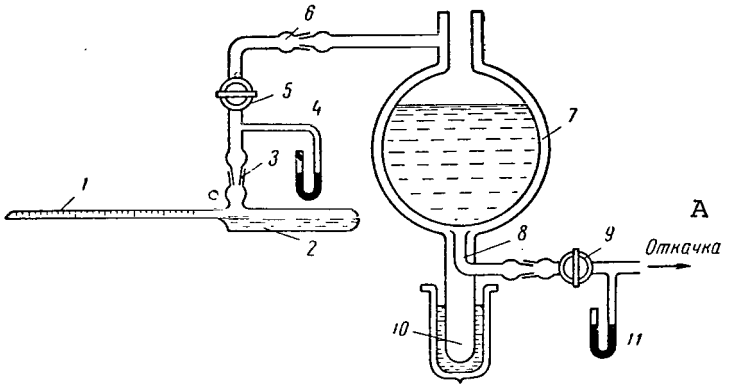

Fig. 49. Device for experiments on Rayleigh depletion of individual hydrocarbon
1. graduated cylinder
2. evaporator
3. evaporator ground-glass joint
4. mercury manometer for regulating pressure in the evaporator
5. overflow valve
6. trap ground-glass joint
7. spherical trap containing liquid nitrogen
8. inlet of fore vacuum line
9. valve of fore vacuum line
10. branch of trap, liquid-nitrogen cooled
11. mercury manometer

Key: A. Evacuation

After the volume of the liquid in evaporator 2 decreases from the initial value V_0 to some specified volume V' through repeated evaporation, the evaporation of the liquid hydrocarbon is halted and the isotopic composition of the initial liquid and residue is measured.

The partition coefficient of isotopes α determining the fractionation of isotopes in the liquid-vapor system is calculated from the formula of Rayleigh depletion:

$$\alpha = 1 + \frac{\lg (1 + \Delta 10^{-2})}{\lg \frac{V_0}{V'}},$$

where Δ is the difference of the isotopic composition of carbon in the initial liquid and in its residue, measured with a mass spectrometer.

Experiments were conducted for three hydrocarbons: benzene, n-hexane, and compressed n-butane.

As is clear from Table 47, we were unable to obtain unique values of α. For large values of the coefficients of Rayleigh compression (that is, the ratios of volumes V_0/V') the extent of separation was not increased as would be expected, but rather began to decrease. As a result, the fractionation coefficients vary as a function of V_0/V' and even showed an inverted value (as in the benzene experiment). Evidently, the failure of the attempts to arrive at an exact value of α is accounted for by the fact that as the degree of evaporation increased, in the residue there were condensed impurities with a different isotopic composition and the test compound. The distortion of the isotopic composition caused by this factor masks the actual value of the isotope effect, though it should be noted that the experiments were conducted with chemically pure (CP) preparations.

TABLE 47. ANALYSIS OF FRACTIONATION OF CARBON ISOTOPES IN INDIVIDUAL HYDROCARBONS IN THE LIQUID-VAPOR SYSTEM

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Experiment number	Hydrocarbon	V_0/V'	ΔC^{13}, %	α
1	Benzene	2	+0.01	1.0004
2	»	4	+0.01	1.0004
3	»	20	−0.01	0.9998
4	n-Hexane	2	0	1.0000
5	»	4	+0.002	1.0002
6	»	20	0	1.0000
7	n-Butane	2	+0.08	1.0009
8	»	10	+0.07	1.0001

Nonetheless, the results make it possible to draw certain conclusions. It is entirely clear that the isotope effects in the liquid-vapor system of an individual hydrocarbon are extremely small. To alter the isotopic composition of the liquid hydrocarbon requires evaporating at least 90-95 percent of its initial volume, which if one has in mind a natural petroleum pool, appears entirely unrealistic. This means that the observed differences in the fractions of the same petroleum and different crudes, which reach several tenths of a percent of δC^{13}, cannot be accounted by the different ability of the hydrocarbons to be evaporated (by the difference in the saturated vapor pressure) or by the different degree of the preservation of the pool in the earth's interior.

Experimental Study of Fractionation of Isotopes in the Thermocatalysis of Oleic Acid

Beginning with the familiar experiments of Engler, various reactions of fat transformation draw attention as one of the possible ways of the formation of petroleum hydrocarbons. As early as 1928, N. D. Zelinskiy and K. P. Lavrovskiy, by conducting experiments with cholesterol (decomposing it in the presence of $AlCl_3$), obtained mixture containing paraffinic and naphthenic hydrocarbons. A similar experiment with oleic acid yielded up to 65 percent liquid hydrocarbons, among which pentamethylene and hexamethylene hydrocarbons were determined. A. F. Frost, using aluminosilicate catalysts and relatively low temperatures of catalysis (100-250°C), showed that the laboratory analysis of hydrocarbons can be conducted in conditions closely approximating those of natural conditions. Subsequently, A. A. Petrov, A. I. Bogomolov, and many other investigators /178 studied in detail products of the thermocatalysis of saturated and unsaturated fatty acids at different temperatures, for different types of catalysts, and so on.

Noting that the thermocatalytic transformation of lipids, in the view of most investigators, underlies the petroleum-forming process and that laboratory thermocatalysis of fatty acids, as is assumed, closely simulates the natural process, we undertook to study the isotopic composition of carbon in the products of thermocatalytic transformation of oleic acid. This work was done by V. G. Shirinskiy. Fractions obtained by S. D. Pustil'nikova were used, who had conducted a corresponding experiment on the supervision of A. A. Petrov. From the description by S. D. Pustil'nikova, the experiment was conducted in a 18-liter autoclave with a mixer. Undergoing analysis were 4 kg 98 percent oleic acid and 12 kg aluminosilicate catalyst with protonic acidity. The experiment lasted 50 hours at 200°C. The yield of the catalysate at the end of the experiment was about 70 percent of the initial oleic acid. The catalysate was extracted from the mixture with benzene. Some of the transformation products were not extracted and remained on the catalyst in the form of condensation products.

The catalysate was a dark oily liquid. The hydrocarbons were separated from the oxygen-containing reaction products in columns containing grade ASK silica gel. The hydrocarbons were washed with ether, and the rest of the compounds was an alcoholic-benzene mixture. In the experiment a total of about 800 g hydrocarbons was obtained. Monocyclic (Ar I), bicyclic (Ar II), and polycyclic (Ar III) hydrocarbons were separated chromatographically. The fraction containing the methane and cyclomethylene hydrocarbons was treated with carbamide. In several cases, a complex was formed, from which hydrocarbons were isolated (n-paraffinic). To determine the ratio of hexamethylene and pentamethylene hydrocarbons, the fraction underwent a two-stage dehydrogenation in the liquid phase over a 20 percent platinum catalyst by a method developed by A. A. Petrova et al. The results of measuring the isotopic composition of the six-membered naphthenes (6-Na) were obtained in practice by

TABLE 48. RESULTS OF ISOTOPIC ANALYSIS OF PRODUCTS OF THERMOCATALYTIC CONVERSION OF OLEIC ACID (IN PERCENT)

Fraction*	Total hydrocarbon of fraction			Hydrocarbons forming carbamide complex		Nondehydrogenable residue Me+Na-fraction		Monoaromatic dehydrogenable products		Biaromatic dehydrogenable products		Aromatic hydrocarbons					
				n-Me		i-Me+5-Na		6-NaI		6-Na II		Ar I		Ar II		Ar III	
	Bromine nr.	Yield of hydrocarbon part	δC^{13}	Fraction yield	δC^{13}	Fraction yield	δC^{13}	Fraction yield,	δC^{13}	Fraction yield	δC^{13}	Fraction yield	δC^{13}	Fraction yield	δC^{13}	Fraction yield	δC^{13}
Kerosene 210—330° C	15.0	11	—	None	—	30	—	9	—2.45	3	—	36	—2.53	22	—2.62	None	—
Gas oil 330—355° C	11.5	18	—2.52	»	—	16	—2.47 ** —2.50	15	—	7	—2.50	48	—	6	—2.49	9	—2.63
Oil distillate 355—455° C	22.0	32	—2.55	3.3	—2.46 **	12	—2.65	7	—2.55	5	—2.53	33	—2.58 **	16	—2.46	23	—
Oil, residual 455° C	16.0	33	—2.61	1.0	—	16	—	9	—	5	—	29	—2.58	9	—	31	—

* Yield of gasoline fraction for hydrocarbon portion -- 6 percent; low-boiling hydrocarbons were not analyzed because of gasoline and petroleum ether being used in the experiment as extractants.

** Results were obtained in a duplicate experiment with an aprotonic catalyst.

the isotopic analysis of the aromatic dehydrogenisate of the corresponding fraction. The residue of the methane-naphthenic fraction was a mixture of isoparaffinic and nondehydratable five-membered naphthenic hydrocarbons (i-Me + 5-Na).

Results of the isotopic analysis are given in Table 48. The initial oleic acid was characterized by $\delta C^{13} = -2{,}51$ percent. Unfortunately, several of the components vital to setting up the isotopic balance (unreacted portion of oleic acid, oxygen-containing compounds of a catalysate, condensation products in the catalyst, benzene fraction of the hydrocarbons, and the gaseous compounds) were not analyzed. It should be noted only that the yield of gases that, as to be expected, were substantially enriched in the light isotope was low, since the pressure in the autoclave during the experiment remained virtually unchanged. /180

These data afford the conclusion that the distribution of carbon isotopes in the thermocatalytic products differs markedly from their distribution in the corresponding fractions of natural crude oils. In some cases these differences are fundamental.

1. Normal paraffinic hydrocarbons formed via thermocatalysis are the isotopically heaviest fraction, while the normal paraffinic hydrocarbons in crudes (especially in the kerosene-gas oil-oil fraction) are the isotopically lightest fraction.

2. In natural samples, polycyclic (Ar III) aromatic hydrocarbons are markedly enriched in the heavy carbon isotope. There is a tendency toward depletion of the aromatic fraction in the light isotope with increase in cyclicity. In aromatic products of thermocatalysis, this tendency was not observed. Measurement in the gas-oil fraction of the isotopic composition of the polycyclic aromatic fraction (Ar III) gave a δC^{13} value corresponding to the highest enrichment in the light isotope among the aromatic fractions.

3. In natural crudes naphthenic hydrocarbons are isotopically lighter than aromatic. In the products of thermocatalysis, the isotopic composition of either is approximately the same, and in terms of the mean value of the total of analyses, the aromatic hydrocarbons proved to be isotopically lighter than the naphthenic.

It is assumed that the first intermediate product of the thermocatalytic transformation of oleic acid is cyclopentane ketone [95]. Then the ring is enlarged with formation of six-membered cyclomethylene hydrocarbons and the dehydrogenation of the latter into aromatic. During this process isotope fractionation can occur at the stage of incomplete dehydrogenation, where owing to the isotope effect determined by the small difference in the rates of dehydrogenation at the C^{12}-H and C^{13}-H bonds the aromatic hydrocarbons can be slightly enriched in the light isotope. This was actually observed experimentally, which confirms the existing

concepts of the mechanism of the thermocatalytic synthesis of hydrocarbons. However, it was found that this mechanism cannot be extended to natural conditions: the distribution of carbon isotopes in structural groups of petroleum hydrocarbons shows that natural aromatic hydrocarbons cannot occur through the dehydrogenation of naphthenic.

Obviously, also different is the mechanism of the formation /181
of normal paraffinic hydrocarbons, which in the experiment and in natural conditions have a diametrically opposite isotopic composition. This is confirmed, by the way, also by the negligible yield of normal paraffins during thermocatalysis, while in natural crudes they are one of the most widespread hydrocarbon classes.

Thus, there is a substantial deviation in the distribution of carbon isotopes in the corresponding fractions of petroleum hydrocarbons and in the products of thermocatalysis. Evidently, in contrast to the widely held view, thermocatalytic reactions are not fully adequate to account for the natural process of petroleum formation.

Origin of Petroleum Hydrocarbons

Normal Paraffinic Hydrocarbons

Normal paraffinic hydrocarbons extracted from the methane-naphthenic fractions of Middle Carboniferous and Devonian crude oils of the Krasnokamskoye Deposit, as is clear from Tables 38 and 39, are enriched in C^{12} relative to the mean carbon of the corresponding fractions and represent the class of the isotopically lightest hydrocarbons.

Chapter One examined thermodynamic isotopic fractions of the main classes of petroleum hydrocarbons, including normal paraffinic hydrocarbons. It was established that the β-factors of normal hydrocarbons have the smallest value among the petroleum hydrocarbons, which corresponds to their enrichment at equilibrium in the light carbon isotope.

Thus, the actual isotopic composition of normal paraffins coincides with the composition predicted from considerations of isotopic thermodynamics. This correspondence is of definite value in our understanding of the origin of paraffinic hydrocarbons in crude oils. The intramolecular distribution of isotopes corresponding to thermodynamic isotopic factors is attained, as was indicated above, during the biosynthesis of organic matter. This accounts, in particular, for the relative enrichment in the light isotope of aliphatic structures among the biochemical constituents of organic matter. The fact that this correspondence occurs in petroleum hydrocarbons once again indicates that the initial material for

normal paraffinic hydrocarbons was primary aliphatic compounds of organic matter.

The following rule can be formulated. If the isotopic composition of individual hydrocarbon or hydrocarbon class corresponds to the value of its thermodynamic isotopic factor (that is, compounds /182
have low β_{Σ}-factors are relatively enriched in the light isotope), then with strong support we can speak of the direct inheritance of the given hydrocarbon structure from the corresponding structural form of the organic matter. If this correspondence does not occur, then it is more profitable that the hydrocarbon was formed through successive chemical reactions, that is, the hydrocarbon structure is not associated with any analogous structure of the initial organic matter.

From the extrapolation formula

$$\beta_{\Sigma_{300^\circ C}}(C_nH_{2n+2}) = \frac{1}{n}[4{,}5672 + 1{,}1520(n-4)]$$

presented in Chapter One it follows that as the molecular weight is increased, some depletion of the normal paraffins in the light carbon isotope must occur. However, this is not observed in nature. From Tables 38 and 39 it is clear that normal paraffins boiling at temperatures of 150-300°C in one case (Krasnokamskoye Deposit, square 207, D3) were found to be isotopically heavier ($\delta C^{13} = -2{,}96$ percent) than higher-molecular paraffins boiling at temperatures of 300-500°C ($\delta C^{13} = -3{,}00$ percent), while in another case (Krasnokamskoye Deposit, square 21, C_2b + vr) they were isotopically lighter ($\delta C^{13} = -3{,}05$ percent and $\delta C^{13'} = -2{,}98$ percent, respectively). The fraction of low-boiling normal paraffinic hydrocarbons (60-150°C) was not isolated.

From these data no correlation can be seen in the distribution of isotopes associated with the molecular weight of normal paraffins. But it can be established indirectly that generally there is some increase in the content of the light isotope in the higher-molecular paraffins. This is indicated by the high concentration of C^{12} in solid paraffins from a number of deposits (Table 49). In addition, as shown by a study of the isotopic composition of low-temperature fractions, as a rule the methane-naphthenic constituent is enriched in the light isotope with increase in boiling point. True, besides normal paraffins, the methane-naphthenic fraction contains isoparaffinic and naphthenic hydrocarbons, which have an isotopic composition differing from that of normal paraffins, therefore the given variations in the isotopic composition of methane-naphthenic hydrocarbons belonging to different temperature fractions can be caused by the different ratio of the normal paraffinic, isoparaffinic, and naphthenic hydrocarbons in these fractions. But the results of a combined analysis of the chemical and isotopic composition of methane-naphthenic fractions (see Tables 41-46) showed that the

tendency toward enrichment of the higher-boiling fractions in C^{12} is due rather to the corresponding enrichment are precisely the paraffinic hydrocarbons in this isotope.

TABLE 49. ISOTOPIC COMPOSITION OF SOLID PARAFFIN IN SEVERAL CRUDES OF THE PERMIAN URAL AREA /183

Deposit	Age of deposits	Test interval, m	Density of petrol g/cm³	Paraffin in petr. %	δC¹³, %	
					petrol.	paraffin
Krasnokamskoye, sq. 21	C_2b+vr	1120—1128	0,849	4,44	—2,93	—3,10
Tanypskoye, sq. 64	C_2b	1044—1058	0,877	4,21	—2,79	—2,93
Sivinskoye, sq. 2	C_2b	1316—1337	0,895	5,07	—2,93	—3,06
Tanypskoye, sq. 21	C_1tl	1408—1412	0,875	3,10	—2,83	—3,01
Tukachevskoye, sq. 1	C_1jsp	1715—1726	0,874	4,88	—3,01	—3,00
Lazukovskoye, sq. 5	C_1jsp	1758—1760	0,908	7,06	—2,98	—3,00
Tanypskoye, sq. 103	C_1t	1457—1468	0,881	2,98	—2,81	—2,95

Thus, if for an entire class of normal paraffinic hydrocarbons the correspondence between thermodynamic isotope factor and actual isotope composition is characteristic, which serves as an indication that the paraffinic hydrocarbons were inherited as a whole from the aliphatic structures of the organic matter, comparing the observed isotope distribution in hydrocarbons having different molecular weights within the same class of normal paraffins with the theoretically predicted distribution does not reveal this correspondence. Therefore, the isotope distribution in paraffinic hydrocarbons of different molecular weights is caused by processes not associated with the nature of the original matter.

It should be noted that by starting from isotopic data we reached the same conclusions that were reached by other methods of studying paraffinic hydrocarbons. In particular, numerous investigations in recent years have studied correlations in the distribution of even and odd normal paraffins in Recent and ancient sediments and crude oils. As we know, predominating in living organic matter are fatty acids with an even number of carbon atoms, generally 14, 16, 18, and 20 carbon atoms. During decarboxylation of these fatty acids (removal of CO_2) normal hydrocarbons can be formed that have, respectively, 13, 15, 17, and 19 carbon atoms in the chain. If the normal paraffins derived from fatty acids, then among them there must markedly predominate odd hydrocarbons chiefly with the above-indicated number of carbon atoms.

Studies by E. Bray and E. Evans, J. Cooper and E. Bray, P. Abelson, P. Parker, D. Lawler, and W. Robinson established that in sediments there is a predominance of even fatty acids and odd normal paraffins (Table 50). This means that actually, saturated fatty acids were the precursors of normal paraffins.

TABLE 50. RATIO OF EVEN AND ODD NORMAL FATTY ACIDS AND PARAFFINS IN RECENT AND ANCIENT SEDIMENTS [182] /184

Sample	Age	Fatty acids		Paraffins	
		Obs. series	CPI_a	Obs. series	CPI_p
Recent sediment 45-150 cm	< 22 000 yrs	$C_{12}-C_{34}$	8.39	$C_{14}-C_{35}$	4.78
Recent sediment 10-80 cm	< 10 000 yrs	$C_{14}-C_{32}$	9.00	$C_{16}-C_{33}$	2.57
Recent sediment 500-555 cm	< 30 000 yrs	$C_{14}-C_{32}$	8.40	$C_{15}-C_{35}$	2.13
Breccia	Pliocene	$C_{14}-C_{34}$	3.18	$C_{19}-C_{34}$	1.16
Shale	Miocene	$C_{13}-C_{36}$	2.22	$C_{14}-C_{35}$	2.18
Oil shale	Eocene	$C_{10}-C_{33}$	1.85	$C_{12}-C_{33}$	2.38
Mowri shale	Cretaceous	$C_{12}-C_{32}$	2.05	$C_{13}-C_{35}$	2.21
Lamar limestone	Permian	$C_{10}-C_{34}$	1.11	$C_{14}-C_{27}$	0.92
Hiss shale	Carbon.	$C_{14}-C_{33}$	4.34	$C_{13}-C_{33}$	1.01
Chatta-nuga shale	Devonian	$C_{10}-C_{32}$	1.23	$C_{12}-C_{31}$	1.05

Remark. The coefficient CPI_8 determines the predominance of total even fatty acids over the total odd fatty acids, and CPI_p refers to the predominance of total odd paraffins over total even paraffins.

However, in the most ancient sediments the predominance of odd alkanes over even is smoothed over to a large extent. In crudes, the ratio of either class becomes virtually the same, and as we know they contain a high level of normal paraffins having lower (C_6-C_{18}) and higher (C_{20}-C_{40}) molecular weights than among alkanes that correspond to the most widely distributed types of fatty acids. Thus, obviously, if as a whole normal paraffinic hydrocarbons are genetically associated with the aliphatic material of organic matter, their distribution by molecular weights depends on the subsequent chemical transformations.

The mechanism of chemical transformations, in addition to all else, must satisfy the observed isotope distribution.

J. Cooper and E. Bray [137] proposed the following scheme in explanation of the gradual smoothing of the ratio of even and odd paraffins and fatty acids in the more ancient sediments:

$$(1)\ RCH\begin{matrix}=O\\ -OH\end{matrix} \rightarrow RCH_2^{\cdot} + CO_2 + H^{\cdot}$$

$$(2)\ RCH_2^{\cdot} - \begin{matrix}\xrightarrow{R'H} RCH_3\\ \xrightarrow[[O]]{} RC\begin{matrix}=O\\ -H\end{matrix}\end{matrix}$$

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From the first reaction there is a loss in CO_2 and a formation of an intermediate radical. The latter can enter into reaction either with the hydrogen donor, leading to formation of a hydrocarbon, or else with the oxidizing reagent, then the fatty acid is reformed, but with the number of carbon atoms one fewer than in the initial fatty acid.

Reproduction of the cycle with the new fatty acid leads to the formation of a smaller high-molecular hydrocarbon, and the step by step to the equalizing of the content of even and odd aliphatic structures. The weakness of this scheme is the necessity of reaction (1), which at temperatures characteristic of the bedding of sedimentary rocks is thermodynamically unacceptable. But if one turns away from this, one can easily see that the Cooper-Bray scheme is satisfactory from the isotopic standpoint. By cleavage of CO_2 with the kinetic isotope effect, the hydrocarbons of reduced molecular weight formed are enriched in C^{13}.

It is interesting to note the following. The primary fatty acid formed by biosynthesis in living cells must, by the rule laid down above, be characterized by an intramolecular distribution of isotopes corresponding to the value of its internal thermodynamic isotopic factors. Carbon in the carboxyl groups of fatty acids, as shown by calculations given in Chapter One, is enriched in the heavy isotope relative to the carbon in aliphatic radicals. Carbon in a normal paraffin formed by decarboxylation of the primary fatty acid will be enriched in C^{12} through the loss of isotopically heavy carbon of the carboxyl group.

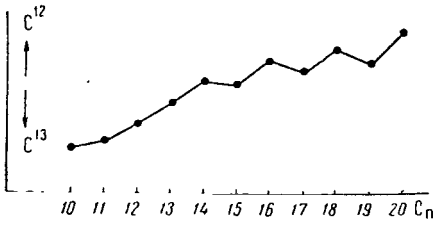


Fig. 50. Assumed distribution of carbon isotopes in normal paraffinic hydrocarbons formed in reactions following the Cooper-Bray scheme

In secondary fatty acids formed via reaction (2), that is, abiogenically, the intramolecular distribution of isotopes is close to the equiprobable, therefore decarboxylation of a secondary fatty acid no longer leads to enrichment of the aliphatic radical in the light isotope. Moreover, through the kinetic isotope effect some enrichment of the corresponding paraffin in the heavy isotope is possible. /186 With each new repetition of the cycle described by reactions (1) and (2), the paraffin with reduced molecular weight formed will progressively be enriched in C^{13}. Ultimately, the pattern shown in Fig. 50 must be observed in the isotope distribution.

Considering that among natural fatty acids we find mostly compounds with 14, 16, 18, and 20 carbon atoms, it must be expected that normal paraffins with 13, 15, 17, and 19 carbon atoms will

have a lighter isotope composition than other hydrocarbons. If the Cooper-Bray cycle is preceded by the dimerization of fatty acids, the foregoing is also true of normal paraffins with 27, 29, 31, and 33 carbon atoms. Accordingly, the foregoing finds an explanation and, it must be assumed, a confirmation in the highly interesting observation by D. Welte [232], who has established a difference (approximately by 0.04 percent) in even and odd paraffinic hydrocarbons of petroleum in the C_{23} - C_{36} range.

The genesis of high-molecular solid paraffin also represents a separate problem. Some investigators believe that solid paraffin is a derivative of high-molecular lipids of the wax type. However, as noted by A. F. Dobryanskiy, "... there is far from enough of these compounds to account for the existence of crudes with 10-15 and even 20 percent solid hydrocarbons" [55]. It is also maintained that high-molecular paraffins may have formed through the dimerization of fatty acids. N. B. Vassoyevich and G. A. Amosov [9] noted that the "predominance of fatty acids through the pairing of molecules closely accountsfor the predominance in sediments and juvenile rocks of n-alkanes -- C_{27}, C_{29}, and C_{31}, with the predominance among the fatty acids of C_{14}, C_{16}, and C_{18} containing nearly half as many carbon atoms." But it should be noted that in the mixture of high-molecular hydrocarbons in petroleum, a prominant position is represented by hydrocarbons containing from 30 to 40 carbon atoms. In ceresins in fact (high-molecular isoalkanes), the number of carbon atoms in the molecule varies from 36 to 55.

Another point of view is that the high-molecular paraffins are the products of the synthesis of normal alkanes having a lower molecular weight. A. F. Dobryanskiy wrote as follows on this subject: "The experimental verification of thermodynamic transformations of various petroleum fractions and of normal paraffin showed that paraffin is not formed during thermocatalysis under any conditions" [55]. And further, "If it is assumed that a certain type of initial matter or certain conditions of transformation made it possible for biradicals to be generated, then this at once accounts for the difference in the content of solid hydrocarbons for different crudes.... If it is recalled that both synthetic gasoline and polyethylene result from the chain interaction of biradicals of the type $-CH_2-$ or $-CH_2-CH_2-$, then it is logical to assume that petroleum hydrocarbons were also obtained by some similar mechanism" (p. 70).

A. F. Dobryanskiy and other investigators proposed a mechanism /187 for the formation of solid paraffins via ".... the cleavage from two initial hydrocarbons of one ethane molecule and the formation of an alkane having increased molecular weight" [99]. However, this mechanism contradicts isotopic data. In this case the high-molecular hydrocarbon, losing the C^{12} isotope through cleavage of the low-molecular fragments of the ethane type would be isotopically heavier than the initial hydrocarbons.

Correlations in the distribution of carbon isotopes in normal paraffins find an explanation if we turn to reactions in which olefins participate. But the formation of olefins at low temperatures is characterized by a rise in the isobaric-isothermal potential and, therefore, are thermodynamically forbidden.

Below is examined in detail a chemical model of petroleum formation that provides for energy transfer in a conjugate system of organic matter -- solid phase of rocks through free radical exchange. By this principle, the generation of a weakly conjugated active radical of the H or CH_3 type occurs not in the system of the compounds of the organic matter, but at the wall of the crystalline phase of country rock. A reaction in which an active free radical participates culminates in the formation of a strongly conjugated radical, which saturates the free valency at the wall. The difference in the energies of conjugation remains in the reacting system. This method provides for energy transfer from the solid phase to the system, and as a result in the system endothermal reactions occur as if they had taken place at high temperatures.

Bearing in mind this mechanism of the process, it is permissible to examine reactions in which olefins are formed at low temperatures:

$$(3)\ R-(CH_2)_x-CH_3+H^{\cdot} \rightarrow R(CH_2)_y-CH_3+CH_3-$$
$$-(CH_2)_z-CH=CH_2+C_2H_5^{\cdot}.$$

Through the generation in the reaction products of the more strongly conjugated radical, formation of an olefin with a high level of free energy proves to be thermodynamically possible.

For example, for the following concrete reaction

$$\begin{array}{lccccc} & CH_3-(CH_2)_{10}-CH_3+H^{\cdot} & \longrightarrow & CH_3-(CH_2)_5-CH_3 & + & CH_3-CH_2+C_2H_5^{\cdot} \\ \Delta Z^{\circ}_{298} & (+6{,}6) & & (+43{,}9) & (+0{,}2) & (+15{,}0)\ (+24{,}0) \end{array}$$

the free energy balance $\Delta Z^{\circ}_{298} = -11{,}5$ kcal, that is, the reaction occurs with a considerable reduction in the level of free energy even at 25°C.

The radical-conjugated reaction can also follow another pathway: /188

$$(4)\ CH_3-(CH_2)_x-CH_3+H^{\cdot} \longrightarrow CH_3-(CH_2)_y^{\cdot}+CH_3-(CH_2)_z-CH_3.$$

The composite result of both reactions is the formation of a low-molecular saturated compound, generation of a strongly conjugated radical, and the formation of an olefinic hydrocarbon.

Olefins in a medium containing radicals rapidly enter into a polymerization reaction following the scheme

$$CH_3-(CH_2)^{\cdot}_x \xrightarrow{CH_3-(CH_2)_z-CH=CH_2} CH_3-(CH_2)^{\cdot}_{(x+z-3)} \longrightarrow$$
$$\xrightarrow{CH_3-(CH_2)_z-CH=CH_2} CH_3(CH_2)^{\cdot}_{x+2(z+3)}$$

and so on. Up to the breaking of the chain, we have

$$CH_3-(CH_2)^{\cdot}_{x+n(z+3)} + CH_3-(CH_2)^{\cdot}_y \longrightarrow CH_3-(CH_2)^{\cdot}_{x+y+n(z+3)}-CH_3^{\cdot}.$$

As a result, hydrocarbon chains with a large number of carbon atoms corresponding to solid paraffins can be obtained. Thus, processes of the subdividing of molecules and the synthesis of higher-molecular compounds can develop simultaneously by the scheme of radical-conjugated reactions.

Now let us examine what the isotope distribution must be in reaction products of this type. Thermodynamic isotopic factors of olefin are characterized by relatively low values. Thus, the β-factor of ethylene is close to the β-factor of ethane. Therefore, low-molecular olefins will be enriched in the light isotope relative to the higher-molecular hydrocarbons of petroleum approximately to the same extent by which gaseous hydrocarbons are enriched in the light isotope (ethane and propane). Olefins with a large number of carbon atoms will increasingly approximate in isotopic composition the initial compound, but will not become heavier than it. Therefore, on the average olefins will be marked by an increased concentration of C^{12}. Since a radical of the $C_2H_5^{\cdot}$ type formed via the scheme of reaction (3) in turn is enriched in C^{12}, the third product of reaction (4) -- a hydrocarbon molecule with lower molecular weight -- will be enriched in the heavy carbon isotope. The process of polymerization with the participation of olefins naturally will lead to enrichment of the synthesized high-molecular paraffins in the light isotope.

Thus, the distribution of carbon isotopes in hydrocarbons of different molecular weights proves to be in accordance with the observed pattern.

Study of the isotopic composition of normal paraffins affords the conclusion that the initial material for hydrocarbons of this class were aliphatic compounds of the organic matter, and the subsequent transformation of the compounds both in the direction of low- /189
molecular as well as high-molecular paraffinic hydrocarbons followed the mechanism of radical-conjugated reactions.

Attention should be directed at the fact that in reactions (3) and (4) a radical of the $R-CH_2$ type is produced, which in the Cooper-Bray scheme is formed in reaction (1) which is unfavorable thermodynamically. In this respect it appears to us that the Cooper-Bray reaction must be considered as a scheme of one of the mechanisms for the realization of the radical-conjugated reactions.

Isoparaffinic Hydrocarbons

Measurement of the isotopic composition of isoparaffinic hydrocarbons in the 150-300° and 300-500°C fractions of Devonian petroleum from the Krasnokamskoye Deposit (square 21) shows an unexpectedly high content of C^{13} compared with normal paraffins from the corresponding fractions. As follows from Table 39, isoparaffinic hydrocarbons are 0.18 percent heavier than normal paraffinic hydrocarbons and are close to aromatic hydrocarbons in isotopic composition. The difference between the normal and isoparaffinic hydrocarbons is quite large. If enrichment of isoparaffins in C^{13} is a general property of petroleum hydrocarbons, it is not easy to give this fact a simple explanation.

This does not follow from thermodynamic arguments. For example, isomerization of n-pentane into isopentane is accompanied by the following change in the isotopic bond numbers:

$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3 \quad (\beta_i = 1.130) \\ CH_3-CH_2-CH_2-CH_2-CH_3 \longrightarrow CH_3-CH_2-\underset{\displaystyle |}{CH}-CH_3 \\ \beta_i = 1.130 \;\; 1.149 \;\; 1.150 \;\; 1.149 \;\; 1.130 \qquad \beta_i = 1.130 \;\; 1.149 \;\; 1.166 \;\; 1.130 \end{array}$$

The isoalkane carbon with which the side CH_3-group is associated has a larger β_i-factor (that is, at equilibrium it is characterized by a higher concentration of C^{13}) than the carbon of the CH_2 group in the normal chain. However, this is compensated by the reduced β_i-factor of the side CH_3 group (β_i = 1.130).

As a result, the β_Σ-factors determining the isotopic composition of compounds as a whole are virtually the same:

$$\beta_\Sigma(n\text{-}C_5H_{12}) = \frac{1}{5}\sum \beta_i(n\text{-}C_5H_{12}) = 1.142;$$

$$\beta_\Sigma(i\text{-}C_5H_{12}) = \frac{1}{5}\sum \beta_i(i\text{-}C_5H_{12}) = 1.141.$$

Hence it follows that hydrocarbons of normal structure and iso- /190
structure formed in the equilibrium process must have the same isotopic composition. In particular, the same isotopic composition must occur in normal and branched hydrocarbon chains as part of the initial material.

If it is assumed that normal hydrocarbons are obtained from hydrocarbons of isostructure through cleavage of the side groups during the petroleum-forming process or transformation of crudes, then normal hydrocarbons must be enriched in the heavy isotope. In this case carbon characterized by a low β_i-factor (1.130) is removed, and the β_Σ-factor of the normal hydrocarbon skeleton therefore rises (in the case of isopentane examined above -- from β_Σ = 1.141 to β_Σ = 1.146). The kinetic isotope effect leads to an even greater enrichment of the normal hydrocarbon in the heavy isotope.

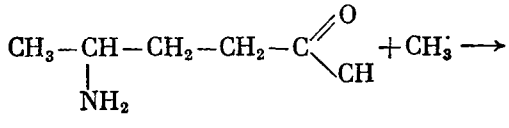
Thus, the distribution of carbon isotopes in normal and isoparaffinic hydrocarbons indicates at least that the normal hydrocarbons in petroleum in bulk could not have been formed through the corresponding isostructural hydrocarbons. This is very important. We recall that essentially the problem of the ratio of normal and isoparaffinic hydrocarbons in crudes consists in that, from the viewpoint of chemical thermodynamics, paraffinic hydrocarbons formed at relatively low temperatures (to 300-400°C) must be nearly entirely represented by isostructural compounds and only at high temperatures -- by the normal varieties.

Accordingly, experimental syntheses of hydrocarbons at relatively low temperatures, for example by thermocatalysis (150-300°C) of fatty acids, leads to formation of entirely or predominantly paraffinic hydrocarbons in the paraffinic fraction, and at high temperatures, for example, in the Fischer-Tropsch process -- normal paraffins. However, in natural crudes that are unconditionally low-temperature formations there is a noticeable predominance of precisely the normal paraffinic hydrocarbons. Accordingly, the hypothesis develops that the "primordial" possibly actually contained chiefly isoparaffins, while the content of normal alkanes increases with greater progression of the transformation of petroleum [24, 55]. Isotopic data, as we have seen, contradict this.

From studying the fractionation of isotopes in the above-considered experiments on the thermocatalysis of oleic acid, normal hydrocarbons were obtained relatively enriched in the heavy carbon isotope. In this case actually a small amount of normal hydrocarbons could have occurred from isostructural hydrocarbons. The difference observed here in the pattern of the distribution of carbon isotopes in natural hydrocarbons and in the products of thermocatalysis confirms the position that normal paraffinic hydrocarbons in natural conditions did not form through branched paraffins. As for the opposite process, that is, transformation of normal hydrocarbons into isoparaffinic, obviously simple intramolecular isomerization also did not lead to the enrichment of isoparaffins in the heavy isotope. Moreover, since the energies of activation of the reactions are somewhat higher for molecules containing C^{13} isotopes, we could have expected enrichment of isoparaffins in the light isotope. /191

It can be represented that isoparaffinic hydrocarbons were formed through the substitution of heteroatomic side groups of organic compounds by hydrocarbon groups.

Isoparaffins of this origin can be enriched in the heavy carbon isotope:



$$\longrightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3+CO_2+NH_2^{\cdot}.$$

But then normal and paraffinic hydrocarbons must be formed predominantly from different starting material. However, in many crudes quite a stable ratio of normal and branch hydrocarbons is observed, which generally indicates their genetical relationship.

The predominance of normal hydrocarbons in crude oils, in our view, stems from the pseudothermochemical character of the radical-conjugated reactions. This same point of view plausibly explains the observed distribution of carbon isotopes in paraffinic hydrocarbons. Probably, isomerization processes are linked to dissociative radical reactions. If in normal hydrocarbon cleaves a low-molecular fragment, then at the same time evidently the residual radical is isomerized before it stabilizes into a molecule having a lower molecular weight. This can be associated, for example, with an increase in the energy of conjugation of the unpaired electron in the branched radical compared to a radical with normal structure. In this case, through the loss of the isotopically light fragment (for example, the CH_3 group), in the isoparaffinic molecule formed the concentration of the heavy carbon isotope rises.

The foregoing is analogous to the assertion that during the radical-conjugated reactions (3) and (4) examined in the preceding section (as applied to normal paraffins), the compound of lower molecular weight that was formed is represented (at least partially) by isostructural hydrocarbons. And an increase in the number of fragmentations experienced by the same molecule leads to its enrichment in the heavy isotope and to an increase in the degree of branching. We recall that due to the nature of the preparative method used, the isotopic data we obtained deal mostly with branched isoalkanes. Hence it also follows that the relative concentration of isoalkanes must increase in low-molecular fractions in which the concentration of the heavy isotope must rise. Both situations actually occur in crude oils. /192

It must be assumed that the content of isoparaffinic hydrocarbons under certain conditions must rise in crude oils of ancient generation. Recently I. B. Kulibakina [72] recorded the results of an analysis of the ratios of n-paraffinic and isoparaffinic hydrocarbons in crude oils from deposits of the Upper Proterozoic and Lower Cambrian of the southern part of the Siberian Platform (Markovskaya and Krivolukskaya areas) and the Middle Cambrian of the western margin of the Russian Platform (Krasnoborskaya area). The crude oils analyzed are of the methane type (Me 66-68 percent, Na

9-25 percent, Ar 3-11 percent), belonging to the category of the highly transformed crude oils. However, predominant in their composition are isostructural hydrocarbons. The ratio of isoalkanes to normal alkanes is 1.14-1.7.

As to the mechanism by which high-molecular isoparaffinic hydrocarbons (ceresins) were formed, we can state what was said with respect to the solid normal paraffin. Since polymerization, as indicated above, is associated with the incorporation into the structure of a high-molecular compound of isotopically light olefins, ceresins must be somewhat lighter than the low-molecular isoparaffins. But since polymerizations in this case occurred in isotopically heavy isotopes, the ceresins must be heavier than the high-molecular normal paraffin. Solid paraffins of isostructure are characteristic, as we know, of naphthenic crudes. So it is of interest to note that in the Bavlinskaya crude from the Sivinskoye Deposit, which is predominantly naphthenic in composition, the isolated solid paraffin was found to be heavier than the overall petroleum, in contrast to all the other analyzed crudes of Permskaya Oblast where paraffin on the average is much lighter than the petroleum.

Naphthenic Hydrocarbons

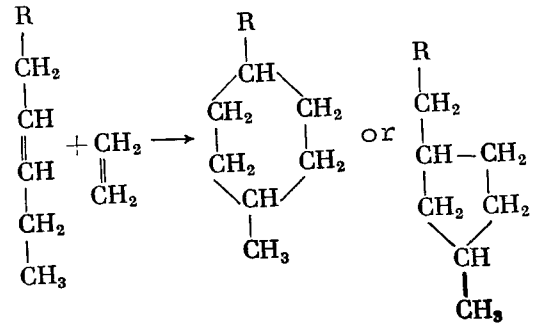
Naphthenic hydrocarbons are close to hydrocarbons in the methane-naphthenic fraction overall, as to isotopic composition. Here they are isotopically somewhat heavier than normal paraffinic hydrocarbons, but lighter than isoparaffinic.

It is quite significant that naphthenic hydrocarbons differ in /193 isotopic composition from aromatic hydrocarbons, and by a higher content of C^{12}. This fact is even more noteworthy in that the thermodynamic isotopic factors (β-factors) characterizing carbon atoms present both as part of aromatic as well as cyclomethylene rings are virtually identical (see Chapter One). The latter signifies that if the naphthenic and aromatic hydrocarbons were the products of the cyclization of some single initial material, they should have the same isotopic composition, on the average. Actually, as we have seen, this is not so, which means that in the crudes they had different precursors, that is, they were genetically linked to different initial compounds of the organic matter. It should be recalled that in experiments on the thermocatalysis of oleic acid when the cyclomethylene and aromatic hydrocarbons formed had a single carbon source, on the average they acquired an identical isotopic composition.

It is suggested [18] that the most suitable compounds as the starting material for cyclomethylene hydrocarbons of petroleum are the unsaturated lipids, while aromatic hydrocarbons evidently inherit predominantly finished aromatic structures of the organic matter.

The light isotope enrichment of naphthenic hydrocarbons compared with aromatic suggests as well that natural aromatic hydrocarbons could not have formed through the dehydrogenation of cyclomethylene hydrocarbons. The rejected premise occupies quite an important position in the system of concepts according to which the naphthenic hydrocarbons are the primary, that is, they correspond to the least-transformed crude oils, while the methane and aromatic hydrocarbons are symmetrical products of the redistribution of hydrogen: in the first case -- hydrogenation of naphthenic hydrocarbons, and in the second case -- dehydrogenation. Dehydrogenation of naphthenic hydrocarbons into aromatic cannot lead to the heavy isotope enrichment of the latter, if we have in mind the thermodynamic isotope effects (in view of the equality of the β-factors of the cyclomethylene and aromatic hydrocarbons). Rather, the reverse is true: dehydrogenation of naphthenic hydrocarbons must lead to some enrichment of the aromatic hydrocarbons in the light isotope, taking note of the possible kinetic effect characterizing the breaking of C-H bonds. It can also be stated that cyclomethylene hydrocarbons as well could not have formed through the hydrogenation of aromatic hydrocarbons. This example probably is significant as added proof that the possibility of obtaining given petroleum hydrocarbons in laboratory conditions still does not indicate that the corresponding reactions actually occurred in nature.

Judging from the isotopic composition of the carbon of naphthenic hydrocarbons, most likely they resulted from processes occurring according to a mechanism of the Diels-Alder reaction type. In this case first we assumed that contained in the initial organic material were unsaturated compounds, for example, unsaturated fatty acids, of which the most widespread are oleic, linolic, and linoleic. Further, if we neglect the possibility of reactions between the unsaturated organic acids as such, the environment must have contained low-molecular olefins. Then the cyclization reactions occurred with a low activation energy and at low temperatures (down to room temperature) without the participation of a catalyst, for example, according to the scheme [55] /194



The mechanism for the appearance of the olefinic hydrocarbon through reactions of radicals has already been discussed. Its isotopic composition in accordance with the value of the β-factor must be characterized by the same content of C^{12} as the composition of the paraffinic hydrocarbons, since the substitution at the carbon atom of one CH bond ($L_{C+H} = 0.028$) and one C-C bond ($L_{C=C} = 0.046$) with a C=C bond ($L_{C=C} = 0.076$) in practice does not lead to a change in the β-factor.

The isotopic composition of unsaturated fatty acids, as shown by experimental data, on the average coincides with the isotopic composition of saturated fatty acids, which serve as the initial material for paraffinic hydrocarbons. Therefore, the above-indicated reaction led to the formation of naphthenic hydrocarbons with an average identical isotopic composition as that for the paraffinic hydrocarbons.

Some polycyclic structures in organic matter of the steroid type contains cycloalkane rings, which may have, as is assumed, been the precursors of the naphthenic and hybrid hydrocarbons of petroleum. D. Anders and W. Robinson [116] studied in detail these constituents in bitumens from Green River shales. They isolated 52 cycloalkanes, /195 whose structures were identified by comparing their mass spectra with the mass spectra of several possible initial compounds of organic matter. Twenty-one compounds had a fragmentational characteristiclike data of tetraalkyl-substituted cyclohexanes that could have originated from carotinoid pigments. Six other cyclohexanes had a mass spectrum like the spectrum of alkyl-substituted hexahydroindanes, whose precursors were possibly the indane moiety of vitamin D. The mass spectra of eight other cycloalkanes afford grounds for proposing a structurelike alkyl-substituted steranes, probably originating from the residues of plant steroids. Seventeen remaining cycloalkanes (three tricyclic and 11 pentacyclic) form mass spectra resembling that of the hydrocarbon skeleton of pentacyclic triterpenoids and may have originated from them.

Thermodynamic isotopic factors of cycloalkanes, as follows from the direct quantum-statistical calculation of the β-factor of cyclohexane and the calculation of the β-factors of cyclomethylene structures based on isotopic bond numbers (see Table 28), have a value close to the β-factors of aromatic hydrocarbons. This means that the cyclomethylene structures formed via biosynthesis must have been enriched in the heavy isotope to the same extent as the aromatic structures. This further means that naphthenic hydrocarbons of this origin in crude oils must have an isotopic composition that on the average is same as for aromatic hydrocarbons and differs toward the side of greater content of C^{13} from that in paraffinic hydrocarbons.

However, the results of studying the isotopic composition of the corresponding petroleum hydrocarbons showed that this is not

the overall pattern: on the average, naphthenic hydrocarbons are close to paraffinic and differ by their higher content of C^{12} from that in aromatic hydrocarbons. This means that most petroleum naphthenic hydrocarbons were formed not from finished cyclomethylene structures of organic matter, in particular the above-listed biochemical constituents, but probably through cyclization reactions of unsaturated aliphatic structures. However, it is entirely possible that the inherited polycyclic structures represented at least some of the high-boiling naphthenic and hybrid petroleum hydrocarbons. Possibly, this was caused by the enrichment in C^{13} of the methane-naphthenic constituent of the high-boiling fractions of several crude oils analyzed (see Figs. 44-48).

Attention must also be given to the fact that the analysis of the isotopic composition of the carbon in naphthenic hydrocarbons of crudes from the deposits of the Permskaya Oblast gave for the middle fraction (150-300°C) δC^{13} = -2.93 percent, that on the average is close to δC^{13} for the Me-Na fractions (δC^{13} = -2.96 percent), and differs from the latter for the aromatic constituent (δC^{13} = -2.70-2.89 percent). At the same time, in the high-boiling fraction (300-500°C), the isotopic composition of naphthenic hydrocarbons is characterized by δC^{13} = -2.86 percent, while δC^{13} = -2.95 percent for the methane-naphthenic fraction, and -2.81 to -2.86 percent for the aromatic. /196

Aromatic Hydrocarbons

Aromatic hydrocarbons are relatively enriched in the heavy carbon isotope. From the data in Tables 38 and 39 it follows that the heavy aromatics within the limits of the same temperature fraction are more enriched in C^{13} in the lighter aromatics. As was noted, aromatic hydrocarbons of the Ar I type are a fraction predominantly of monocyclic compounds, Ar II -- of bicyclic, and Ar III -- of bi-tricyclic. Therefore, it can be concluded that the isotopic composition of aromatic hydrocarbons changes with increase in cyclicity toward the side of higher concentration of C^{13}.

An increase in the content of the heavy carbon isotope in higher-cyclic hydrocarbons agrees entirely with the values of their thermodynamic isotopic factors. While the β-factor of benzene is 1.153, the β-factor of naphthalene is 1.156, and the β-factor of phenanthracene is 1.158 (see Table 28). Thus, it is precisely the distribution of isotopes in aromatic hydrocarbons of different cyclicity which is actually observed in practice that proves to be thermodynamically probable.

In the aromatic fraction, besides these specific aromatic rings there are also the naphthenic rings and aliphatic radicals linked to the aromatic rings.

The fraction isolated as Ar I consists of compounds with a single aromatic ring, and as the length and the number of the side substituents increases the boiling point rises. Benzene, toluene, xylenes, ethyl benzene, and isopropyl benzene fall into fraction Ar I (60-150°C). Diethyl-substituted and dipropyl-substituted homologs of benzene fall into the fraction Ar II (150-300°C). Monoaromatic hydrocarbons that have three substituents in which the number of carbon atoms in the radical is more than two fall into the fraction Ar I (300-500°C).

Biaromatic hydrocarbons have boiling points about 200°C (naphthalene -- 218°C, methyl naphthalene -- 241°C, biphenylmethane -- 260°C, and so on) and, in the absence of a large number of substituents, fall into the heavy aromatic fraction -- Ar III (150-300°C).

The aromatic hydrocarbons that have three connected or condensed rings employed at temperatures of about 300°C (stilbene -- 305°C, anthracene -- 340°C, phenanthrene -- 340.2°C, and so on) and fall into the fraction Ar III (300-500°C).

Bicyclic hydrocarbons containing aromatic and naphthenic rings (hybrid) for mostly into the fraction Ar II.

Fig. 51 shows the distribution of structural types of aromatic hydrocarbons in the fractions analyzed; the values of C^{13} of the carbon in fractions are given as the average for the two crude oils analyzed, and for each analyzed fraction -- the C^{13} calculated on the assumption concerning the corresponding structural makeup of the fraction. The calculation was carried out based on the following considerations. The mean δC^{13} of normal paraffinic hydrocarbons for the two crudes is -3.00 percent, taken as the characteristic of the isotopic composition of the carbon in the aliphatic radicals (R). The symbol R stands for the presence on the average of three carbon atoms in the radical. The content of more than four to five carbon atoms in the side chain is uncharacteristic of natural hydrocarbons. The mean δC^{13} of the naphthenic hydrocarbons, for the two crudes, is -2.90 percent, taken as the characteristic of the isotopic composition of the carbon in aliphatic rings incorporated in hybrid of aromatic hydrocarbons. It is customarily assumed that in accordance with the thermodynamic isotopic factors of aromatic compounds predicting a rise in the C^{13} content with increase in cyclicity, the carbon of the monoaromatic ring is characterized by $\delta C^{13} = -2.84$ /198 percent, the aromatic dicycle -- $\delta C^{13} = -2.80$ percent, and the aromatic tricycle -- $\delta C^{13} = -2.75$ percent.

As we can see from Fig. 51, there is a satisfactory agreement between the experimentally measured and calculated δC^{13} values for the corresponding fractions. This signifies the applicability of the additivity principle employed here, in other words, the isotopic composition of a complex hydrocarbon can be obtained by summing the isotopic compositions of its constituent structural

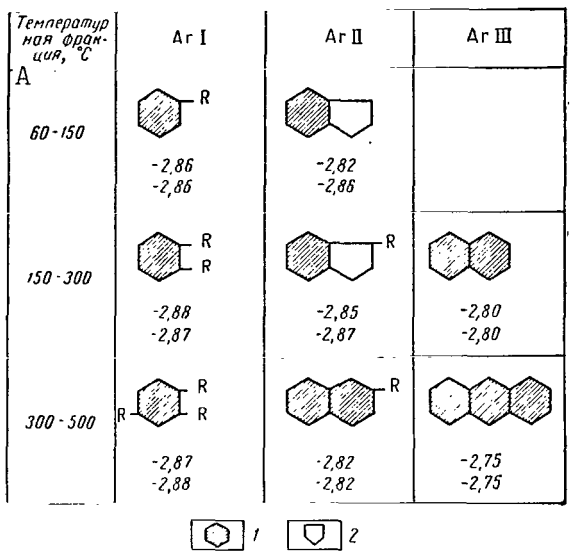


Fig. 51. Comparison of measured and calculated δC^{13} values for various structural forms of aromatic hydrocarbons in petroleum
1. aromatic ring
2. naphthenic ring
R. paraffin radical. The figures in the illustration are δC^{13} (in percent) measured (upper) and calculated (lower)
Key: A. Temperature fraction, °C

elements taken in the corresponding atomic proportions. This also confirms the genuineness of the intramolecular isotope effects, that is, it shows that the interatomic distribution of isotopes within a hydrocarbon molecule is nonequiprobable. /197

Based on concepts of intramolecular isotope effects, we can approach more closely to an understanding of the mechanism of heavy isotope enrichment, and from there -- to the mechanism of the formation of high-cyclic aromatic hydrocarbons.

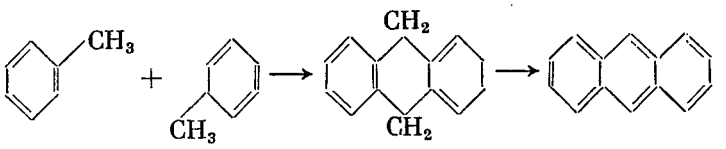
As was shown in Chapter One, benzene has a molecular thermodynamic isotopic factor β_Σ of 1.153. The methyl substituted homolog of benzene -- toluene -- is somewhat enriched in the light carbon isotope (β_Σ = 1.152). But this is obtained by means of a low value of the β_i-factor characterizing the carbon of the radical (β_i = 1.130). As for the aromatic ring of toluene, it is isotopically heavier than benzene (the thermodyanamic isotopic factor is 1.155). In di-substituted homologs of benzene this tendency intensifies. For example, xylenes must overall be isotopically lighter than benzene and toluene, but the aromatic ring of xylene is even more highly enriched in C^{13} than the ring of toluene, and so on. This judgment is valid not only for the case of hydrocarbon substituents, but also for heteroatomic radicals. Depending on the nature of the radical, its β_i-factor will change, but in any case the aromatic ring in which the atoms have bonds to side groups exhibits a greater tendency toward concentration of the heavy isotope than the unsubstituted benzene ring.

Thus, if the condensation of aromatic rings occurs through the preliminary rupture of side groups, the compound that is of higher cyclicity will be isotopically heavier than the initial

compounds. The opposite is also true; decyclization accompanied by the alkylation of the aromatic compounds with lower cyclicity that are formed leads to their enrichment in the light isotope.

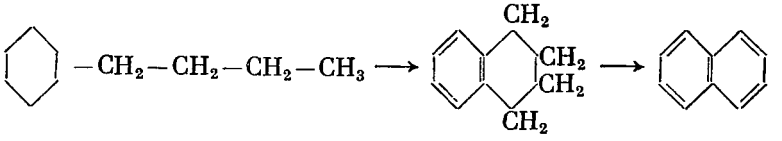
It should be stressed that we are talking in all cases about a given rearrangement of already existing aromatic rings. Reactions presupposing the formation of aromatic rings from material of non-aromatic nature appears much less probable in lighter isotopic data.

Thus, when benzene homologs undergo diorthocondensation anthra- /199
cene can be formed:

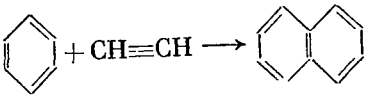


However, here the polyaromatic ring proves at least to be not heavier (isotopically) than the mononuclear compound, since one of the rings inherits the isotopically light carbon of the methyl groups.

Equally just as improbable is the reaction of dicyclization through the joining of the end of the side chain to the aromatic nucleus:



We know that biaromatic structures are easily formed when benzene condenses with olefins:



Usually reactions of this type for natural conditions are rejected on the principle that there are no olefins in petroleum. However, as was emphasized above, the radical character of the petroleum formation reactions make the origination of olefins at intermediate stages quite possible. But olefins, just like saturated aliphatic compounds, are relatively enriched in C^{12}, therefore the bicyclic hydrocarbons formed with the isotopically lighter than the monoaromatic hydrocarbons.

Thus, when an attempt is made to link isotopic data with any concept on the neoformation of aromatic rings, difficulties spring up. This of course applies not only to polycyclization, but in general to the possibility of aromatic structures originating from organic compounds that are nonaromatic. The entire problem needs

further careful experimental study. Given available data, it appears more natural that aromatic structures of petroleum hydrocarbons are predominantly inherited from aromatic structures of organic matter during whose biosynthesis the intramolecular distribution of isotopes was formed, satisfactorily accounting for the correlations observed.

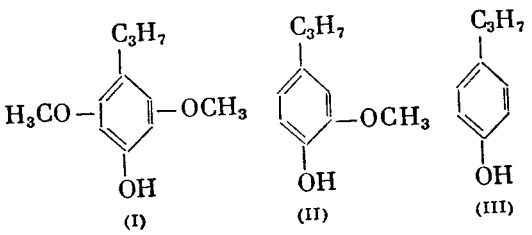
Aromatic rings in organic matter undergoing humification originate both from biogenic phenol compounds as well as through the aromatization of carbohydrates and the melanoidine reaction [82]. /200

Phenol compounds are a widely distributed class of compounds participating in the structure of several biochemical constituents of living matter. Most widespread of them is lignin, forming up to 30 percent of the biomass of the higher plants. Lignin and lignin-like compounds are also found in algae [81]; aromatic rings are contained in aromatic acids (tyrosine, and phenylalanine), and hydroxybenzoic acids, and appreciable number of which can be isolated from marine plankton [195].

By their structure, biogenic phenol compounds stand closer than any other cyclic compounds of organic matter to the aromatic hydrocarbons of petroleum. Also essential is the fact that in the isotopic sense the genetical relationship between aromatic hydrocarbons and phenols appears most substantiated.

Phenol groups that are monomeric segments of lignin usually consist of an aromatic ring with a hydroxyl substituent, with one or several methoxyl substituents, and with a side radical, often of hydrocarbon structure.

According to S. M. Manskaya and T. V. Drozdova [82], wood lignin can contain monomeric units of the syringic type (I), compounds of the phenylpropane series with the guaicyl structure of the aromatic ring (II), and monomers of p-hydroxylpropane (III) structure:



The last (III) compounds are characteristic of lignin in herbaceous plants. In general, characteristic of lignin in lower plants are compounds with a low methoxyl number.

For aromatic rings of the above-presented compounds, β_Σ(I) = 1.171, β_Σ (II) = 1.167, and β_Σ (III) = 1.163. This can easily be calculated by using the method outlined in Chapter Two. These values are relatively small. Compounds of this type must be among the isotopically light constituents in organic matter. The β_Σ-factors of phenol compounds are close to the β_Σ-factors calculated for the aromatic hydrocarbons. At the same time, these values are higher than the β_Σ-factors characterizing at the aliphatic compounds /201 in organic matter. Measurement of the isotopic composition of lignin in natural samples showed that its carbon actually is enriched in the light isotope compared to most other constituents, but is isotopically heavier than the carbon in lipids. To the same extent, aromatic hydrocarbon in petroleum on the average are isotopically heavier than paraffinic.

This isotopic similarity affords grounds for assuming that aromatic structures of the phenolic series may have been the direct precursors of the aromatic hydrocarbons in petroleum. To this it must be added that lignins and ligninlike compounds, along with lipids -- precursors of paraffin-naphthenic hydrocarbons -- are among the biochemical constituents that are most difficult to decompose. Opening up of the aromaticrring requires very high energies of evacuation. Different reactions of substitution, addition, and condensation occur much more readily, but the total number of aromatic rings here remains unchanged (of course, if the process occurs in mild conditions). A. F. Dobryanskiy pointed to the "nondestructability" of aromatic rings. It is therefore natural to assume that the evolution of organic matter led ultimately to the segregation of aromatic structures in the form of aromatic hydrocarbons.

We emphasize once again that although among the petroleum hydrocarbons aromatic compounds are marked by an increased C^{13} content, with respect to the mean carbon in organic matter they are considerably enriched in C^{12}. Therefore, the starting material for aromatic hydrocarbons could have been only isotopically light constituents of organic matter (exhibiting relatively low β_Σ-factors). Lignin as a whole satisfies this condition. Among its monomeric units, structures with a minimum methoxyl number are marked by the lowest β_i-factors. These structures, as indicated above, are characteristic of lower plants. Accordingly, it can be concluded that it is precisely the organic matter in lower plants that basically serve as the source for the aromatic hydrocarbons in petroleum.

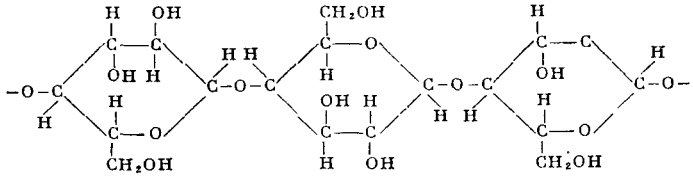
Aromatic rings in living matter not only are contained in ligninlike compounds, but are also part of the makeup of aromatic amino acids, and hormones, and can be isolated as a constituent part of the lipid fraction. Since the β_Σ-factors of biologically synthesized aromatic rings have relatively low values, the compounds in which they are present must be enriched in the light isotope. Actually, as shown by analyses of the isotopic composition of carbon in individual amino acids, the aromatic amino acids

tyrosine (δC^{13} = -2.28 percent) and phenylalanine (δC^{13} = -2.27 percent) are marked enriched in the light isotope compared to the other amino acids, in particular alanine (δC^{13} = -1.18 percent), glycine (δC^{13} = -0.77 percent), threonine (δC^{13} = -1.64 percent), serine (δC^{13} = -1.68 percent), and aspargic acid (δC^{13} = -1.56 percent). Only isoleucine (δC^{13} = -2.22 percent) is enriched in C^{12} to the same extent as aromatic acids; by virtue of its structure, isoleucine has a β_{Σ} -factor that is close to the β-factors of tyrosine and phenylalanine. It should be noted that the aromatic amino acids represent approximately 6-7 percent of the total number of amino acids in marine plankton. /202

Since the biosynthesis of aromatic rings includes the mechanism of their enrichment in C^{12} carbon (just as in the biosynthesis of lipids), it is natural to expect that also other constituents which have as their basis aromatic rings, for example, cyclic terpenoids, will have an isotopic composition characteristic of the aromatic hydrocarbons in petroleum.

The concepts of a direct genetical relationship between the aromatic hydrocarbons in petroleum and the aromatic structures of organic matter finds support also as the result of a comparison of the abundance of several individual biochemical constituents and the corresponding structural isomers of aromatic hydrocarbons. For example, of the three possible isomers of methylisopropylbenzene in crude oils, on the average 1-methyl-4-isopropylbenzene and 1-methyl-3-isopropylbenzene are distributed one order of magnitude higher; their structures correspond to the natural classes of monoterpenoids, and the 1-2-isomer, for which no corresponding terpenoid is known [191].

In addition to their aromatic rings inherited from living matter, fossil organic matter includes cyclic structures originating during diagenesis. These structures can be formed through the aromitization of cellulose:



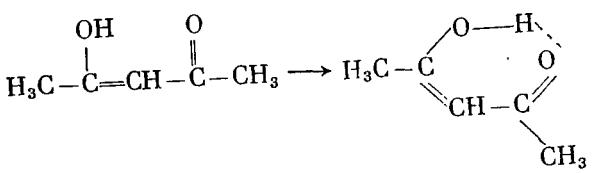
Calculation of the β_{Σ}-factor for the carbon of the ring present in the monomeric unit of cellulose gives the value 1.183 (see Table 28), which considerably exceeds the values of the β_{Σ}-factors characterizing phenol groups. Therefore, aromatic structures formed on the basis of cellulose were proved to be isotopically heavy and differing in isotopic composition from most petroleum hydrocarbons.

Measurement of the isotopic composition of the carbon in polysaccharides in organic matter shows that they are enriched overall in the heavy carbon isotope (δC^{13} = -1.92 percent) compared with lignin (δC^{13} = -2.31 percent), but to a lesser extent than protein /203
(δC^{13} = -1.75 percent) and pectin compounds (δC^{13} = -1.67 percent). Here the isotopic composition of hemicellulose is characterized by δC^{13} = -1.87 percent, and that of cellulose by δC^{13} = -2.24 percent.

Considering that in the high-boiling fractions of petroleum and tars there is often contained isotopically relatively heavy aromatic hydrocarbons, it can be assumed that some of the aromatic compounds were formed through material of the cellulose type. But aromatic hydrocarbons of this origin doubtless are secondary in importance. We must also consider that cellulose exceptionally facilely undergoes hydrolysis and is the paramount object of microbiological attack, therefore most of the cellulose, as for carbohydrates in general, is lost in the first stages of humification of the organic matter.

The formation of melanoidines, which as is assumed served as the precursors of humic acids, resulted from the reaction of amino acids with sugars. The structure and mechanism of formation of the melanoidines has not been conclusively established. However, based on qualitative reactions, pyrole and aromatic rings have been found in the structure of melanoidine molecules [82].

It is highly probable that the initial act along the path of cyclization was the formation of intramolecular hydrogen bonds of the type, for example, found in the enolic form of β-diketones:



Energetically, hydrogen bonds in these compounds, which are often called chelates, are extremely strong. Subsequent reactions of substitution can lead to the formation of a valency-saturated ring. Hydrogen bonds, both intra- as well as intermolecular, are formed as we know through the reaction of a highly protonized hydrogen atom that is present, for example, in the hydroxyl group or in an amino group, and an electronegative atom (O, N. F, Cl). Therefore formation of hydrogen bonds and chelates in the products of the melanoidine reaction, that is, in the reaction products of amino acids and carbohydrates appears plausible.

The presence of an intramolecular hydrogen bond is usually established by inspecting infrared spectra and the spectra of combination scattering. Accordingly, it is of interest to know that recently F. Stevenson and K. Goh [223] analyzed several humic acids and fulvic acids, which they classified into three types in relation to spectral characteristics. They concluded that the variation in the intensity of individual absorption bands in humic acids of different types is due to the fact that with increasing extent of humicification there are losses in the COOH groups and change in the position of the C=O and OH groups, which are converted from free of weakly H-bond positions into more strongly chelate forms. /204

But participating in the formation of chelate (containing hydrogen bond) rings are carbon atoms either part of the makeup of functional groups or else bond to heteroatoms of the functional groups. Carbon atoms in this position are marked by extremely high β_i-factors. In other words, the carbon of cyclic structures resulting through melanoidine reactions must be considerably enriched in a heavy isotope and on the average must differ markedly from the carbon in aromatic hydrocarbons in petroleum.

Probably, cyclization processes occurring during the humidification of organic material lead directly to the formation of the hydrocarbon skeleton of hexagonal cells of carbonaceous matter condensed through C-H bonds, but not aromatic hydrocarbon rings.

Asphalt-Tar Constituents

Asphalt-tar constituents are high-molecular compounds of irregular structure. Asphaltenes form with petroleum hydrocarbons a colloidal solution and are precipitated when there is a high excessive low-molecular hydrocarbons, which underlies their analytical determination. The tars are separated from petroleum by means of absorbents.

Tars and asphaltenes are among the nonhydrocarbon compounds. It is precisely in the composition of these constituents that most of the oxygen, sulfur, and nitrogen in crude oils is concentrated, which opens up the possibility of turning to the isotopic analysis of these elements in the study of the problems of the genesis of tariy substances. In particular, as shown by S. P. Maksimov, N. A. Yeremenko, R. G. Pankina, V. L. Mekhtiyeva, T. A. Botneva, and so on, by comparing isotopic composition of sulfur in crude oils and organic matter as well as in various species of mineral sulfur, one can approach the resolution of the question of its origins in crude oils and the facial conditions of the sedimentation basin. In studying the origin of asphalt-tar constituents, carbon isotopy evidently is capable of yielding no less interesting results than the isotopy of sulfur in other heteroelements.

TABLE 51. ISOTOPIC COMPOSITION OF CARBON IN TARS AND ASPHALTENES IN CRUDE OILS FROM THE PERMIAN URAL AREA

Deposit (area)	Stratigraphic complex	Interval, m	Characteristics of crude oil						δC^{13}, ‰		
			Density, g/cm³	Content, %							
				S	N	Tars	Asphaltenes	Paraffins	Crude oil	Tars	Asphaltenes
1	2	3	4	5	6	7	8	9	10	11	12
Golubyatskoye, sq. 109	P_1s	945—960	0.951	3.18	0.45	11.85	5.93	3.22	—2.96	—2.80	—2.82
Pavlovskoye, sq. 272	C_2b	1012—1021	0.884	2.32	0	17.90	3.47	2.67	—2.78	—2.59	—2.52
Sivinskoye, sq. 2	C_2b	1316—1337	0.895	1.88	0	15.25	9.64	5.07	—2.93	—2.71	—2.80
Rassvetovskoye, sq. 1	C_2b	1328—1359	0.906	3.76	0.41	26.98	5.42	3.07	—2.81	—2.70	—2.67
Kasibskoye, sq. 2	C_2b	1395—1503	0.920	1.13	0	20.20	4.62	2.91	—2.95	—2.81	—2.79
Brusyanskoye, sq. 24	C_2b	1603—1624	0.819	0.89	0	4.53	tr.	4.65	—2.84	—2.79	—
Stepanovskoye, sq. 2	C_1jsp	1394—1398	0.861	1.87	0.30	16.01	1.00	7.02	—2.87	—2.58	—2.66
Gremikhinskoye, sq. 112	C_1jsp	1407—1408 1502—1507	0.904	2.63	0.43	22.54	2.07	3.47	—2.94	—2.78	—2.72
Yelkinskoye, sq. 63	C_1jsp	1702—1707	0.803	1.09	0.04	5.05	0	5.85	—2.93	—2.64	—
Troyel'zhanskoye, sq. 15	C_1jsp	1694—1697	0.862	1.78	0.13	9.38	1.46	7.69	—2.84	—2.75	—2.81
Luzhkovskoye, sq. 94	C_1jsp	1612—1615	0.859	1.91	0.21	10.02	0.78	5.36	—3.00	—2.71	—2.72
Tukachevskaya, sq. 1	C_1jsp	1715—1726	0.874	1.63	0.29	14.55	3.02	4.88	—3.01	—2.81	—2.78
Kuz'minskoye, sq. 85	C_1jsp	1720—1740	0.853	1.35	0.22	22.03	1.89	4.22	—2.85	—	—2.57
Lazukovskoye, sq. 5	C_1jsp	1758—1760	0.908	2.38	0	15.72	3.74	7.06	—2.98	2.77	—2.76
Kasibskoye, sq. 2	C_1jsp	1770—1776	0.816	0.69	0	5.44	0	4.0	—2.89	—2.76	—
Ol'khovskoye, sq. 17	C_1jsp	1838—1843	0.816	0.54	0	4.75	0	4.16	—2.92	—	—
Yavinskoye, sq. 1	C_1jsp	2522—2540	0.838	0.27	0.11	3.84	0	4.06	—2.92	—2.75	—
Etyshskoye, sq. 249	C_1t	1384—1405	0.896	2.24	0.31	—	—	—	—2.74	—2.67	—2.74
Nozhovskoye, sq. 6	C_1t	1521—1552	0.902	3.09	0	18.78	2.66	4.87	—2.84	—2.65	—
Aspinskoye, sq. 2	D_3fm	1950—1970	0.895	2.47	0.31	16.75	1.50	3.81	—2.70	—2.70	—2.64
Aspinskoye, sq. 11	D_3fm	2203—2207	0.873	1.49	0.28	13.94	2.37	3.87	—2.75	—2.63	—2.75
Aspinskoye, sq. 8	D_3kn	2222—2226	0.922	2.22	0	22.59	11.64	3.26	—2.64	—2.64	—2.72
Dubovogorskoye, sq. 5	D_3p	2167—2170	0.879	1.85	0	13.77	3.96	2.94	—2.84	—2.66	—2.74
Tartinskoye, sq. 8	D_1	2215—2256	0.909	2.13	0.35	17.55	12.39	3.07	—2.78	—2.62	—2.62
Bezymyannaya, sq. 22	D_3p	2220—2224	0.934	2.68	0.50	24.94	5.82	4.42	—2.78	—2.67	—2.76
Sivinskoye, sq. 1	Rf	2788—2800	0.955	—	—	—	—	—	—3.05	—3.04	—3.02

The advantage of the carbon method is that it makes it possible to compare the isotopic composition of the carbon in tarry substances and other constituents of petroleum, in particular, various structural groups of petroleum hydrocarbons.

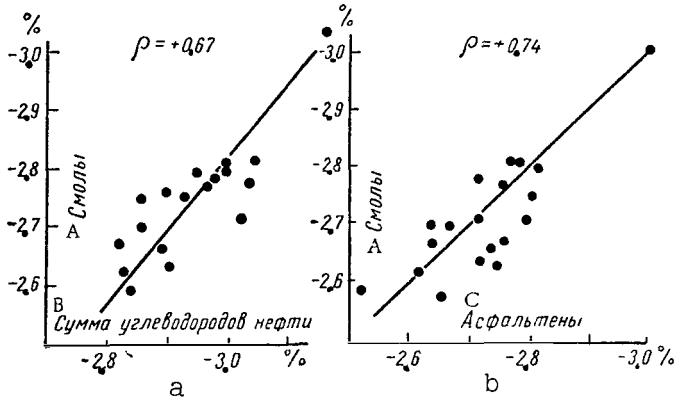


Fig. 52. Comparison of isotopic composition of carbon in tars and total of petroleum hydrocarbons (a), tars and asphaltenes (b) (Permian Ural Area)
Key: A. Tars
B. Total of petroleum hydrocarbons
C. Asphaltenes

As we can see from /206 Table 51, the carbon in tars and asphaltenes is heavier than the carbon in the corresponding crudes. The difference is 0.2 percent, where the isotopic composition of both constituents is very close. It is important to note that enrichment in the heavy carbon isotope of tars and asphaltenes is observed not only in the mean, but also in each individual petroleum sample by approximately the same value.

The isotopic composition, tars approximate polycyclic aromatic hydrocarbons, which in general is in complete agreement with the aromatic character of the tars. Between the isotopic composition of tars and asphaltenes there is a relationship with a high coefficient of correlation (ρ = +0.74), where the regression line is linear and symmetric with respect to the coordinate axes (Fig. 52). Therefore asphaltenes are of the same nature as tars and, evidently, are the product of the further condensation of hydrocarbon structures intrinsic to tars.

If the conversion of tars to asphaltenes is accompanied by the loss of any structural elements, for example, aliphatic radicals, and by an increase in the extent of condensation of the aromatic nuclei, this inevitably would lead, based on the foregoing, to enrichment of asphaltenes in the heavy carbon isotope. The absence of this enrichment proves that asphaltenes in all probablity are the results of the condensation of tarry compounds without essential change in the basis of their structural and elemental composition.

In this respect we come to understand the apparent, somewhat paradoxical fact that, in spite of the high molecular and specific weight of asphaltenes, the ratio of hydrogen and carbon therein is exactly the same as in the tars.

The origin of tarry compounds in different crudes can differ. /207 Let us examine the genetical scheme (Fig. 53). First, it is obvious that we must distinguish tars genetically associated with other hydrocarbons of the given crude from those not thus associated. In the latter case, tarry compounds can be present in petroleum, for example, through their extraction from rock during migration. It is of interest to consider this possibility, since often an analogous mechanism is proposed with respect to paraffins, isoprenoids, and other "shaped" residues of organic matter in crudes.

Obviously, with the absence of a genetical relationship between tars and hydrocarbons of petroleum, it is difficult to expect any correlations between their isotopic composition. But as we can see from Fig. 52, quite a close association has been established for the analyzed crudes of the Permian Ural Area (coefficient of correlation $\rho = +0.67$) between the isotopic composition of the tars and the nontarry portion of the corresponding crudes. The presence of this association indicates the oft autochthonicity of the tars -- their genetical origin in the crudes in which they occur.

Tars can be primary or secondary with respect to crude oils. By secondary tars, we obviously mean tarry compounds formed from petroleum hydrocarbons. In contrast, tars are primary if they may have served as the source of petroleum hydrocarbons. Here the tars isolated from the given crude can be considered either as preserving part of the initial material (parent) or as a by-product of the transformation of this initial material (source).

Since in the crude oils analyzed the isotopic composition of the carbon in tars ($\delta C^{13} = -2.70$ percent) differs markedly from the mean isotopic composition of the carbon in liquid petroleum (δC^{13} /208 $= -2.9$ percent) and all the more so from that of the carbon in petroleum that includes carbon in the gaseous phase ($\delta C^{13} = -3.3$ percent), it can be concluded that tarry compounds cannot be parental for all of the petroleum. Thus, the analyzed tars in this case can relate to the category of primary residual tars (see Fig. 53) or they can be the product of secondary changes in petroleum hydrocarbons.

Starting from the idea of the equilibrium intramolecular distribution of isotopes in biological systems and using the principle of calculating the β-factors by relying on isotopic bond numbers, in principle one can differentiate hypergenetically oxidized organic compounds from primarily oxygen-containing organic compounds. jIn particular, through the isotopic analysis of carbon one can determine the origin of carbon in acidic bitumens and tarry constituents of petroleum.

The isotopic bond number of C-O ($L_{C-O} = 0.055$) is larger than the isotopic bond number of C-C ($L_{C-C} = 0.046$) or C-H ($L_{C-H} = 0.0285$), therefore the more bonds of the C-O type in a biogenetic organic

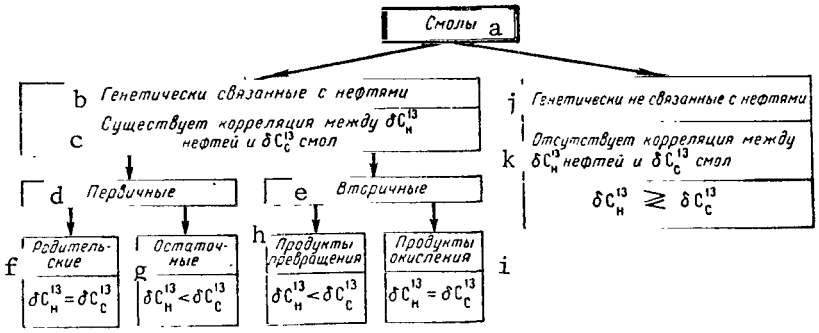


Fig. 53. Genetical scheme of the distribution of tars as a function of their isotopic composition

Key:
a. Tars
b. Genetically associated with crude oils
c. There is a correlation between δC_H^{13} of crudes and δC_C^{13} of tars
d. Primary
e. Secondary
f. Parental
g. Residual
h. Products of transformation
i. Products of oxidation
j. Genetically and associated with crudes
k. There is no correlation between δC_H^{13} of crudes and δC_C^{13} of tars

compound are present for a given number of carbon atoms, the more highly the compound is enriched in the heavy carbon isotope. A compound that has the same number of carbon atoms but does not contain any C-O bonds will be isotopically relatively light. Its oxidation does not lead to a variation in isotopic composition if we neglect the genetic isotope effect, whose realization can promote an even greater enrichment of the oxidized compound in the light isotope. Hence it is clear that under otherwise equal conditions an oxygen-containing organic compound inheriting its oxygen from a biological source will contain a heavy carbon isotope at a higher concentration than a compound that acquired its oxygen from reactions of abiogenic oxidation.

Since in the case of crudes of the Permian Ural Area we are dealing with isotopically relatively heavy tars, it can be stated that they are not the oxidation product of petroleum hydrocarbons.

However, the formation of secondary tars can evidently proceed in another pathway, for example, by polymerization occurring under the effect of external factors, including those in which it is possible that oxidation conditions play a certain role. If this process occurs primarily on the basis of aromatic hydrocarbons, isotopically heavy tars are obtained, which in terms of the isotopic composition of carbon evidently can not be differentiated from primary residual tars (see Fig. 52).

Gas-Dissolved Crude Oils (Condensates)

Correlations in the distribution of carbon isotopes in narrow-temperature fractions gives an explanation for the phenomenon of heavy carbon isotope enrichment of light condensate crudes. By conducting in 1966 an isotopic analysis of several gas-condensate crude oils from Lower Cretaceous Deposits of Western Cis-Caucasus, it is established their marked enrichment in C^{13}: from -2.25 to -2.39 percent (Table 52). As follows from Fig. 31, these figures correspond to the isotopically heaviest crudes, in particular they are comparable with other Low Cretaceous crudes of the Cis-Caucasus. At that time it was difficult to give this finding a specific interpretation. /209

TABLE 52. ISOTOPIC COMPOSITION OF CARBON IN CONDENSATE FROM LOWER CRETACEOUS DEPOSITS OF THE STAROMINSKOYE GAS-CONDENSATE DEPOSIT (WESTERN CIS-CAUCASUS)

Bore hole number	Ratio of gas ($1000\ m^3$) to condensate (tons) in daily flow of bore hole	Perforation interval, m	δC^{13}, %
1	275/22	2102—2122	—2.31
4	291/23	2110—2206	—2.39
7	165/13	2180—2189.4	—2.34
39/9	181/14	2123.5—2160	—2.25

Systematic enrichment in C^{13} of the low-boiling fractions of the crudes (reaching values of 0.2-0.3 percent) render comprehensible the formation of isotopically heavy condensates, since the solubility of low-boiling components in the gases is considerably higher than for high-molecular compounds. Thus, there is no need to seek the cause of the heavy carbon isotope enrichment of the condensates in the special character of the initial material or in the specific mechanism of fractionation of carbon isotopes during formation of the gas-condensate mixture.

As was shown above, paraffinic hydrocarbons of isostructure are marked by considerable enrichment in the heavy carbon isotope

(averaging 0.18 percent) relative to normal paraffins. This indicates one more cause of the C^{13} enrichment of condensates. Branched alkanes dissolve methane much better than normal alkanes of the same molecular weight. As a result, isostructural hydrocarbons accumulate in gas-dissolved crudes, which are easily established when natural pools are analyzed [72].

Thus, enrichment of condensates in the heavy carbon isotope wholly explains their hydrocarbon composition, the substantial predominance of low-boiling hydrocarbons, and also the relatively increased content of isoparaffin hydrocarbons, that is, exactly the constituents that are relatively enriched in the heavy isotope in any crude oils.

Chemical Model of Petroleum Formation /210

Radical-Conjugated Reactions

Considerations dealing with the chemical model of petroleum formation given below derive significantly from the results of analyzing the correlations in the distribution of carbon isotopes in natural hydrocarbons. As was shown above, the interpretation of any observed isotope effects is based on the assumption that olefins have a substantial role in the reaction mechanism. The origination of olefins at low temperatures is assumed to be thermodynamically forbidden. However, it is known that olefins are the most important intermediate reaction product of hydrocarbons if in the system a radical reaction is initiated in some way. Below we examine the problem in a more general form, based on some model that takes into account the energetic aspect of the process.

After studies by A. V. Frost, A. F. Dobryanskiy, F. Rossini, et al., the concepts of the chemical content of petroleum formation were developed mostly in the thermodynamic approach, which was found to be productive at least because it made it possible to remove from consideration chemically unrealistic schemes of petroleum formation.

Essentially, the thermodynamic approach makes it possible to find the directions of the spontaneous change in a chemical system. The chemical system is taken to be a set of components of organic matter or a set of petroleum hydrocarbons whose transformation is then considered as a spontaneous process (without substantial participation of factors that are external with respect to the selected system). This process is caused by the reserve of internal energy in the system and amounts to the redistribution of the chemical potentials in the system, which leads to its minimum free energy.

As we know, hydrocarbons are compounds exhibiting a high level of free energy. In contrast, many heteroorganic formations (fats, amino acids, alcohols, sugars, and so on) have a low free energy level. It can be shown that very frequently the conversion of organic compounds into hydrocarbons at normal temperatures is impossible by means of the internal energy reserve. In several cases the energy balance proves to be highly stressed.

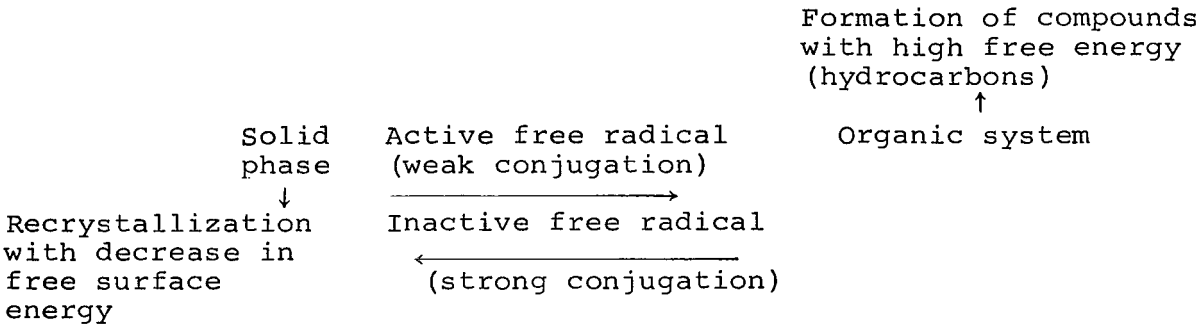
In order for a reaction to be appreciably shifted toward the side of forming a product, there must be approximately a 10 kcal/mole decrease in the isobaric-isothermal potential. Under normal conditions, few spontaneous reactions of hydrocarbon synthesis satisfying this condition occur. In contrast to the widely held view, also among the thermodynamically unfavorable reactions are those in which paraffinic hydrocarbons are formed from high-molecular fatty acids. /211

Only at temperatures of 100-150°C and higher can hydrocarbon formation reactions become thermodynamically admissible. For this reason the familiar schemes of petroleum formation in one way or another relate this process to the action on organic matter of elevated temperatures. Still, in most cases present-day conditions of petroleum deposition and the assumed conditions of its formation do not correspond to the temperatures which appear to be necessary from the thermodynamic standpoint.

When evaluating the direction in which processes are developed in a chemical system, the thermodynamic approach is valid given the condition that the system is adequately isolated, that is, it includes all phases and all components that are in interaction. Many investigators have recognized that the energetic aspect of the transformation of organic matter to petroleum is poorly described by low-temperature thermodynamics. In our view the reason for this is that the petroleum-producing organic matter cannot be regarded as an isolated system.

Thermodynamic analysis also enables us to judge the relative content of particular constituents (regardless of the mechanism of their formation) if the system is in a state of a reversible process, that is, at or near equilibrium. But petroleum hydrocarbons are not an equilibrium system. Far from equilibrium the kinetic factors and the actual mechanism of the reaction become substantial. Accordingly, below an attempt is made not only to develop the principles of an examination of the energetic aspect of the transformation of organic matter somewhat differing from former principles, but also to show, at least in general outline, its mechanism.

Essentially, the model discussed below amounts to the petroleum-forming process being considered within the framework of the energetically conjugate system organic matter -- solid phase of rocks: The latter serves as an inducer of energy, and the organic matter serves as the acceptor.



As a result of the conjugated process, the energy of the solid phase is reduced and the reserve of internal energy of the chemical system is increased, which brings about endothermal reactions of /212 hydrocarbon synthesis. The energy transfer mechanism involves defects in the crystalline structure arising during the geologic evolution of rocks producing at the solid phase surfaces free valencies, leading to the generation of radicals transmitted throughout the bulk. Here in the chemical system reactions occur that are induced by the free radicals. One feature of these radical reactions is that an active, weakly conjugate radical of the H· type is introduced into the system and a strongly conjugate high-molecular radical is reproduced. The difference in the energies of conjugation of the radical entering into reaction and the generated radical remains in the chemical system and is an additional source of energy that can remove the thermodynamic constraints from the reactions of the transformation of organic matter into petroleum.

It should especially be emphasized that here a different meaning is given to the concept of radical reactions (in this case we call them radical-conjugated reactions) than in the case when by radical reaction one means the radical mechanism of chemical reactions.

When we are speaking about a radical mechanism, it is assumed that a pair of free radicals is formed in the reacting system in some way or other, and the reaction (or chain process) of the recombination of a pair of radicals is culminated. In radical-conjugated reactions examined within the framework of the model under discussion, an unpaired radical generated at the wall of the solid phase is introduced into the reacting system. The reaction ultimately ends with the destruction of the radical at the wall.

The formal difference of these types of radical reactions is, in particular, the fact that a reaction whose intermediate stages follow the free radical mechanism can always be written in summary form without radicals.

For example, the sequence of radical reactions

$$C_3H_8 \longrightarrow C_2H_5^{\cdot} + CH_3^{\cdot};$$
$$C_2H_5^{\cdot} + C_3H_8 \longrightarrow C_4H_{10} + CH_3^{\cdot};$$
$$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow C_2H_6$$

reflects the mechanism of the composite reaction

$$2C_3H_8 = C_4H_{10} + C_2H_6,$$

while the radical mechanism of the hydrogenation of ethylene

$$H^{\cdot} + C_2H_4 \longrightarrow C_2H_5^{\cdot};$$
$$C_2H_5^{\cdot} + H_2 \longrightarrow C_2H_6 + H^{\cdot}$$

reduces to the composite reaction

$$H_2 + C_2H_4 = C_2H_6.$$

In radical-conjugated reactions, the radicals serve as independent reagents that cannot be canceled out of the summary reaction, for example: /213

$$C_3H_8 + H^{\cdot} \longrightarrow C_2H_6 + CH_3^{\cdot}$$

The radical mechanism of the reactions has repeatedly been examined as applied to the chemistry and geochemistry of petroleum. Free radicals, the so-called stable, long-lived radicals, were discovered in crude oils [12, 163]. Research attention was concentrated on the favorable kinetics of radical reactions. The reaction of free radicals, as we know, is characterized by low energies of activation, therefore if there is a method for chain initiation, that is, formation of primary radicals, all subsequent stages take place very rapidly. In this case apparently there was an interchange in the application of the energy needed to activate the chemical process. Instead of the excitation of intermolecular collisions, this energy was expended in the generation of free radicals. The difference is only that intermolecular collisions were excited only through heat transfer into the system, while radicals can be generated in different ways. Several investigators, for example, pointed to the possibility of the production of radicals through radioactive radiation. Some variants of the mechanism of heterogeneous catalysis provide for the formation of radicals at the catalyst.

All this, however, has no bearing on the energetic aspect of petroleum formation. The reaction mechanism as such, whether it be radical or catalytic, does not determine either the general direction or the equilibrium concentrations of the reaction products, that is, the parameters that are dictated by the thermodynamics of the process. For example, the equilibrium constant of the above-listed hydrogenation reactions ($H_2 + C_2H_4 = C_2H_6$) and the disproportionation of hydrogen ($2C_3H_8 = C_4H_{10} + C_2H_6$) independently of the radical mechanism of their occurrence is determined by the balance of free energies (isobaric-isothermal potentials ΔZ) of the

components in the composite reaction. In particular, at 25°C, regardless of the mechanism, the reaction

$$2C_3H_8 = C_4H_{10} + C_2H_6;$$
$$\Delta Z^0_{298}\ 2(-5{,}61)\ (-3{,}75)\ (-7{,}86);\ \Delta Z = -0{,}39 \quad \text{kcal/mole}$$

is characterized by approximately equimolar concentrations of the components.

Radical reactions become a factor determining not only the kinetics but also the thermodynamics of the process if the latter takes place in such a way that during the reaction the free valency passes from the active radical characterized by weak conjugation of the unpaired electron to a less active -- strongly conjugated radical.

The concept of energies of radical conjugation was introduced /214 into chemical kinetics by Academician N. N. Semenov. Essentially, it consists of the following. As we know, enthalpy is determined by the energy released in the formation of interatomic bonds, therefore enthalpy is an additive quantity in the sense that it is proportional to the products of the number of the given bonds by the mean energy of these bonds. However, the breaking of the same C-C bond strongly depends on its localization in the molecule. The rupture energy of CH_3-CH_3 bonds is 83 kcal/mole, for C_3H_7-C_3H_7 -- 76 kcal/mole, $C_6H_5CH_2$-CH_3 -- 63 kcal/mole, and CH_2CHCH_2-CH_2CHCH_2 -- 38 kcal/mole, for a mean energy of the C-C bonds -- 84 kcal/mole [106]. The difference between the mean bond energy and the actual energy expended in breaking the bond is determined by the conjugation of the radicals, that is, the bond energy of the unpaired electron in the radical formed.

If during a reaction between components one bond is replaced with another, thermal energy is released equal to the difference in the energies of these bonds. However, reactions are possible in which even though new products are formed, the number and nature of the bonds remain the same. For example: CH_2=$CHCH_2CH_3$ + $CH_3^{\cdot}$ → CH_2=$CHCH_2^{\cdot}$ + CH_3-CH_3. During this reaction one of the C-C bonds in the butylene molecule is broken, but this same bond is produced again when the ethane molecule is formed. It would appear that the reaction has no heat of reaction. However, actually it does and it is equal to the quantity determined by the difference in the energies of conjugation of the electrons in the allyl CH_2=$CHCH_2^{\cdot}$ and methyl $CH_3^{\cdot}$ radicals.

Hence it becomes clear that if an active radical is introduced into a reacting system and is reproduced with a less active radical, the energy equal to the difference of conjugations remains in the systems; this can ensure the carrying out of reactions that are thermodynamically forbidden at the given temperatures (if we consider the reacting system in isolation from sources of radicals).

Let us show this with the following example. The direct decarboxylation of palmitic acid and the formation of the corresponding hydrocarbon at 25°C is thermodynamically forbidden (their reaction cannot occur with increase in the isobaric-isothermal potential ΔZ):

$$C_{15}H_{31}COOH \longrightarrow C_{15}H_{32} + CO_2;$$

$$\Delta Z^0_{298} \quad (-80.0) \qquad (+16.1)\,(-94.3)\ \Delta Z = +1.8 \text{ kcal/mole}$$

But, if the reaction occurs with the participation of an active free radical and the formation of a most strongly conjugated radical, the yield of products becomes possible:

$$C_{15}H_{31}COOH + H^{\cdot} \longrightarrow C_{13}H_{28} + C_2H_5^{\cdot} + CO_2;$$

$$\Delta Z^0_{298} \quad (-80.0)\ (+43.9)\ \ (+14.3)\ (+24.1)\ (-94.3);$$

$$\Delta Z = -19.6 \text{ kcal/mole.}$$

/215

It can be shown by the example of many other organic reactions that the participation of free radicals as reagents increases by 10-20 kcal/mole the reserve of internal energy of the initial compounds, which makes thermodynamically feasible a broad range of possible reactions of the synthesis of hydrocarbons from organic matter at low temperatures.

Generation of Radicals at Wall

From the foregoing it is clear that the energetic aspect of the process of petroleum formation finds a satisfactory explanation if it is assumed that energy transfer occurs via the exchange of free radicals differing in energies of conjugation. But here we must answer two questions: how do the radicals originate and from where is the energy taken which is transmitted into the reacting system?

The source of free radicals, as indicated by G. M. Panchenkov, are these: 1) thermal decomposition of organic compound; 2) photodissociation; 3) reactions in an electrical discharge; 4) action of metals on organic halogenides; 5) initiating compounds of the type of benzoyl peroxide, tetralin peroxide, hexaphenylethane, diaziminobenzene, and so on; and 6) radiolysis on exposure to alpha-, beta-, and gamma-radiation.

None of these methods are applicable for natural conditions. However, in chemical practice the initiating role of the walls of reaction vessels is well known. By the method of separate calorimetry it was established that the rate of a reaction at walls is considerably higher than in the bulk. In several cases the wall has an inhibiting effect. Wall activity is caused by the fact that the wall serves as a source of radicals and a location for their discharge (death of radicals). The concentration of free valencies per cm^2 of the surface is estimated by the quantity

$10^{13}\ e^{-U/2RT}$, where U is the energy of formation of the unpaired electron at the surface. The transfer of the radical into the bulk takes place through the interaction of a compound with the wall MR + V. → MV + R', where V stands for the free valency. The energy of activation of this process is low. Since U, which has a value of 20-30 kcal, is much smaller than the bond rupture energy, for example, for the C-C bond (84 kcal), the rate of generation of radicals at the vessel wall exceeds by several orders the rate of their formation in the bulk through intermolecular collisions.

It can readily be calculated that from the foregoing expression, when U = 20 kcal and t = 25° C, the number of free valencies per cm^2 of surface area will be about 10^5. This number is not high. However, in an actual crystal there are always defects (owing to the presence of impurities or the mixing of atoms in the interstitial sites), which either themselves are free valencies, or else they promote a reduction in the energy of formation of the unpaired electron. These defects, on migrating into the crystal, reach the surface. The number of defects in the crystal is determined by the number of thermal defects $n = ae^{-b/T}$ plus the number of impurity atoms in the crystal lattice, plus the number of free valencies at the intracrystalline surfaces of dislocations, pits, and microcracks. The total number of defects of all kinds is of the order of $10^{20}\ g^{-1}$. By electron paramagnetic resonance [EPR], 10^{18} radicals per g of material was established at the fresh surface of quartz powder [107]. N. N. Semenov showed that "any active surface in contact with any molecules will to some extent serve as a generator of free radicals. By active, we mean a surface consisting of crystals for which U is much lower than the energy of dissociation of the molecule into radicals, or a surface that has any (perhaps even a high) U, but contains a sufficiently large number of defects)" [106, p. 291]. /216

In nature, the role of the walls of the reaction "vessel" in which the organic matter is transformed is played by the surface of the mineral portion of rocks.

The mechanism of the heterogeneous radical reaction can be represented thusly:

1) $\mathrm{V} + \mathrm{H_2O} \longrightarrow \mathrm{V\,OH} + \mathrm{H}$;

2) $\mathrm{H}^{\cdot} + (\mathrm{OB}) \longrightarrow (\mathrm{VB}) + \mathrm{R}^{\cdot}$;

3) $\mathrm{V} + \mathrm{R}^{\cdot} \longrightarrow \mathrm{V}\,R$;

4) $\mathrm{V\,R} + \mathrm{V\,OH} \longrightarrow \mathrm{ROH} + \mathrm{VV}$.

In the first stage the radical is initiated by means of the free valency V and the chemosorbed compound VOH is formed. Of course, the latter may be not only a water molecule, but any other compound. Further, the reaction is transmitted into the bulk and the above-described radical reaction of the transformation of organic matter (OM) into hydrocarbon (HC) occurs, with the formation of a strongly conjugated, high-molecular radical R·. The third stage is the breakdown of the radical at the wall. Migration to the surface VR and VOH leads to the deposition of the oxidized coke ROH and the annihilation of the free valency. At stage (3), one could represent another process $R^{\cdot} + VOH \rightarrow ROH + V$ with the regeneration of the free valency. However, owing to the strong conjugation of the radical R· it is thermodynamically disadvantageous.

In order for the regeneration of V to be carried out, the process must take place as follows: /217

$$1)\ V + H_2O \longrightarrow VOH + H^{\cdot};$$

$$2)\ H^{\cdot} + (OB) \longrightarrow (VB) + H^{\cdot};$$

$$3)\ H^{\cdot} + VOH \longrightarrow V + H_2O.$$

In this case, we are dealing with the radical mechanism of heterogeneous catalysis. Here the properties of the catalyst remain unchanged, but also unchanged is the thermodynamics of the reacting system at stage (2).

Thus, the understanding of the role of the solid phase outlined here approximates the concept of the role of heterogeneous catalysis.

However, there are major points of difference.

1. The action of the catalyst requires direct contact of the compound with the surface, while radicals are transported from the surface into the bulk. When the surface is filled with chemosorbed compounds, the catalytic process dies out. Radicals can, as shown by the investigation of Z. S. Roginskiy /103/, be transported into the bulk even through a coked-over surface.

2. The activity of the catalyst is nearly exclusively determined by the properties of its surface, in particular, by U. The capacity for generation of free radicals depends on the structure of the crystals overall, for example, on the number of structural defects, impurities, size of micropits, dislocations, and so on. Here not only is the condition of the crystal significant, but also its geologic history during which new defects arise, and so on.

3. During the chemical reaction the catalyst remains unchanged. If the process is accompanied by energy transfer as in this case, inevitably irreversible changes occur in the crystalline phase or, to put it a better way, the irreversible changes in the solid phase are the source of the energy which is transferred into the bulk.

Thus, the generating ability of the solid phase of rocks is intimately bound up with its evolution during geologic time. Rock activity is not limited to the reserves of fresh surface. During the reaction, fairly rapid saturation of the surface with the binding molecules of the reactant set in, therefore catalysts that are extremely efficient in laboratory conditions may be of no geochemical significance.

The production in crystals of free valencies, in particular, defects, and their migration can be caused by decrystallization and recrystallization of rocks, dissolution and secondary mineralization, by the effect of the steadily rising geostatic pressure, by sign-alternating stresses associated with tectonic conditions, and by the effect of temperature, that is, ultimately by the entire complex of factors that determine the process of lithogenesis. /218

Energy Exchange in the System Organic Matter -- Solid Phase

The activity of the surface in the case we are examining is associated with a steady decrease in the free surface energy. Therefore we have to estimate the comparability of the free energy of the crystalline phase with the energy transmitted into the reacting system via radical exchange.

In chemical thermodynamics, the formation of a unit surface area of a body is estimated by the specific total surface energy $\Delta\varepsilon_{hkl}$ (erg/cm^2):

$$\Delta\varepsilon_{hkl} = \Delta\sigma_{hkl} - T\left(\frac{\partial\sigma_{hkl}}{\partial T}\right)_P, \qquad \text{(IV.1)}$$

where σ_{hkl} is the specific surface energy, and the symbol hkl characterizing the crystallographic classification of the face makes allowance for the fact that the specific surface energy differs for different faces.

The change in the total surface energy $\Delta\varepsilon_{hkl}$ per unit volume of the solid phase capable of performing external work, in particular, increasing the internal energy of the chemical system associated

with the solid phase, is obtained by totaling the change in the specific free surface energy $\Delta\sigma_{hkl}$ for all faces of all types of crystals comprising the solid phase:

$$W\sum_{j}^{n} g_j\left[\sum_{hkl}^{m}\Delta\varepsilon_{hkl}j_{hkl}\right]_j=\Delta G-WT\sum_{j}^{n} g_j\left[\sum_{hkl}^{m} j_{hkl}\left(\frac{\partial\sigma_{hkl}}{\partial T}\right)_P\right]_j \qquad \text{(IV.2)}$$

where W is the specific surface of the solid phase (cm^{-1}); j_{hkl} and g_i are, respectively, the statistical weight of the face of a given type in a given type of crystal, and the statistical weight of a given type of crystal included in the solid phase, and the summation is carried out over m -- the number of faces of different types in the given type of crystal and n -- the number of different types of crystals comprising the solid phase.

The energy release during the consolidation and decrystallization of rock is used in increasing the internal energy, more exactly, in increasing the enthalpy if we consider the process at constant pressure:

$$\Delta H_i=\Delta Z_i+T\,\Delta s_i,$$

where Δs_i is the change in the entropy of the chemical system; ΔZ_i is the change in the isobaric-isothermal potential of the chemical system; and ΔH_i is the change in enthalpy.

This ratio pertains to one mole of the compound. Let us introduce the following notation: c is the concentration of the reaction products (hydrocarbons) in the petroleum-producing rock (g/g); δ is rock density; and M is the weight of one mole of reaction product. Then the increase in the enthalpy of the chemical system in terms of the amount of hydrocarbons per unit volume of the petroleum-producing rock will be expressed by the relation /219

$$\Delta H=\frac{c\delta}{M}\Delta Z_i+T\frac{c\delta}{M}\Delta s_i. \qquad \text{(IV.3)}$$

In order that the energy transfer from the surface of the solid phase into the chemical system be sufficient to complete in it the anticipated chemical transformations, the condition $\Delta G\geqslant\Delta H$ must be satisfied. Therefore the following inequality must be met:

$$W\sum_j^n g_j\left[\sum_{hkl}^m \Delta\varepsilon_{hkl}j_{hkl}\right]_j + \underbrace{TW\sum_j^n g_j\left[\sum_{hkl}^m j_{hkl}\left(\frac{\partial\sigma_{hkl}}{\partial T}\right)_p\right]_j}_{\Delta s_{sol}} \geqslant \frac{c\delta}{M}\Delta Z_i + T\underbrace{\frac{c\delta}{M}\Delta s_i}_{\Delta s_{chem}}. \qquad \text{(IV.4)}$$

In the right and left sides there appear expressions, of which Δs_{sol} corresponds to the change in surface entropy per unit volume of the solid phase, and Δs_{chem} corresponds to the entropy change of the chemical system, that is, the reacting compound contained in the same unit volume.

By solving the inequality for ΔZ_i, we get:

$$\Delta Z_i \leqslant \frac{MW}{c\delta}\sum_j^n g_j\left[\sum_{hkl}^m \Delta\varepsilon_{hkl}j_{hkl}\right]_j + T(\Delta s_{sol} - \Delta s_{chem})\frac{M}{c\delta}. \qquad \text{(IV.5)}$$

The second term in the right-hand side is proportional to the entropy change of the isolated system, embracing both the chemical system under study as well as the solid phase. By the second law of thermodynamics, the entropy of an isolated system increases if nonequilibrium heat exchange is present in it. In the conditions of equilibrium heat exchange or the absence of heat exchange, the entropy of an isolated system is constant.

We are considering specifically the latter case, therefore this term of the inequality is equal to zero, and finally we get:

$$\Delta Z_i \leqslant \frac{MW}{c\delta}\sum_j^n g_j\left[\sum_{hkl}^m \Delta\varepsilon_{hkl}j_{hkl}\right]_j. \qquad \text{(IV.6)}$$

From the resulting expression, we can approximately estimate the order of magnitude of a specific surface of the solid phase providing for the energy transfer needed to realize the anticipated chamical transformation. An increase in the isobaric-isothermal potential ΔZ_i required in order for hydrocarbons to form from organic compounds is of the order n·10 kcal/mole; the specific surface energy of the crystals is n·100 erg/cm^2; the concentration of hydrocarbon c in the petroleum-producing rock can be taken as n·10^{-4} g/g; δ = 2.5 g/cm^3; and the mean weight of a grammolecule of petroleum hydrocarbons M $\simeq$ 200 g. Then by Eq. (IV.6), W $\geqslant$ n·10^4 cm^2/cm^3. /220

This value of the specific surface is characteristic of clays, carbonate sediments, and clay sandstones. Well-graded medium-grained sands have W = 300-400 cm^2/cm^3, that is, less than is required by condition (IV.6).

Thus, the reserve of free surface energy of the solid phase for clay rocks is comparable in overmagnitude with the energy absorbed in endothermal reactions of hydrocarbon synthesis.

Dislocations and internal defects in crystals will serve as a source of free valencies; upon their arrival at the surface of crystals, the total energy content of the surface can be considerably increased. Moreover, during geologic time rocks cannot only undergo evolution caused by internal factors, but may also be subject to external influences. The deformation of crystals caused by tectonic stresses repeatedly during the geologic life of a rock lead to a major change in the structure of the solid phase, and an increase in its surface energy and in the actual surface area through crushing and mixing of particles. A similar action can be exerted by stratal water capable of metasomatic recrystallization, leaching, and so on.

Thus, from the point of view of the energy transfer mechanism we are examining, clay rocks are the most promising as petroleum-generating rocks, as well as rocks that have been subjected to intensive processes of recrystallization, for example, reefogenic or dolomitizing limestones.

Pseudothermochemical Character of Radical-Conjugated Reactions

It is essential to note one feature of this process deriving from a comparison of the purely catalytic action of the solid phase with its role as a free energy source.

The catalytic action of the surface consists in lowering the energy of activation of the chemical reaction and, consequently, increasing the reaction rate. Strictly speaking, no reduction in the energy of reaction takes place, but rather the replacement of one stage characterized by a high energy of activation by several stages, each of which differs by lower energies of activation /221 (Fig. 54 a). However, here the character and concentration of the end products do not depend on the participation of the catalyst and are determined only by the ratios of the free energies of the components of the reacting system. Catalysts, in particular, cannot cause a reaction that is thermodynamically forbidden at the given temperature. In contrast to this, a process characterized by energy transfer in the system organic matter - solid phase can permit the occurrence in the reacting volume of this

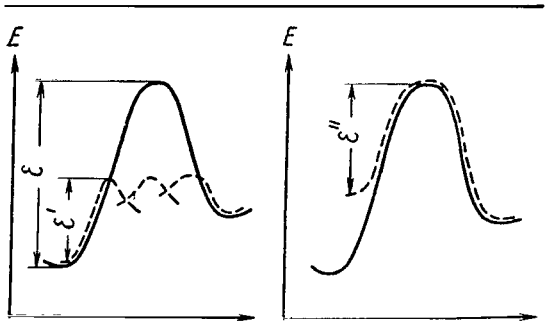


Fig. 54. Change in the path of catalyzed (a) and radical-conjugated (b) reactions

reaction and the formation of products in such ratios that could not be anticipated if we viewed the thermodynamics of the chemical system in isolation from the solid phase. As shown in Fig. 54, in the reaction catalyzed the activation barrier $\varepsilon' < \varepsilon$, is lowered, but remaining unchanged is the enthalpy $\Delta H = \Delta H'$. In the second case, not only is the energy of activation $\varepsilon'' < \varepsilon$, changed, but also the value and even the sign of the enthalpy change (Fig. 54 b).

In the latter case everything takes place as if the reaction temperature had been increased. This means that the reaction realized through energy transfer with the solid phase behaves as a pseudothermo reaction, that is, the direction of the reaction, the nature of the products, and their ratio correspond to the reaction course for a given composition of the initial reactants that would have occurred for the corresponding rise in the temperature of the medium.

This approach is valid, although the process takes place without heat transfer. It should be remembered that the temperature is not a coordinate of thermal action. Entropy s is this coordinate. When heat transfer is present, entropy changes -- -- $ds \neq 0$, and in its absence -- remains constant ($ds = 0$). One criteria in the selection of a physical quantity acting as the coordinate of this interaction is its constancy in the absence of this interaction. We know that temperature can be changed by means of adiabatic (without heat transfer) processes. For example, the temperature of a body can be changed through adiabatic expansion or compression or by adiabatic magnetization or demagnetization, and so on.

Thus, the high temperature yield of the products of a chemical reaction in conditions in which the ambient medium is at a low temperature, can be viewed as an actual process of adiabatic increase in the temperature of the reacting system through the work done by the surface forces of the crystalline bodies. Accordingly, a phenomenon that to some extent appears strange in the chemistry of crude oils finds a satisfactory explanation. The point is that the chemical composition of petroleum in many respects corresponds to high-temperature thermodynamics. For example, in crude oils normal alkanes /222

considerably predominate over isoalkanes. Still, in hydrocarbons formed at low temperatures iso-compounds must predominate. The situation does not change the fact that the initial structures of the organic matter, for example, fatty acids, contain radicals of normal structure, since in the transformation of fatty acids the paraffinic hydrocarbons formed undergo isomerization. Actually, in experiments on the low-temperature transformation of organic acids paraffinic hydrocarbons were produced, but nearly always of isostructure /3, 97/.

There have been numerous attempts to determine the temperature of petroleum formation based on the individual concentrations of hydrocarbons in crude oils. By knowing the free energies of entropy and specifying the PT parameters, one can calculate the equilibrium constants and ultimately the equilibrium ratios of the system components or, by solving the inverse problem, that is, starting from known concentrations, determine the temperature at which they correspond. In the general case this method is not applicable to crude oils, since petroleum hydrocarbons as a whole do not form an equilibrium system.

However, D. Rossini, for example, at one time showed that isomers of C_9 alkylbenzenes in different crudes are in highly stable ratios, where their relative concentration corresponds to the equilibrium temperature of 450° C. Similar thermodynamic calculations for C_8 alkylbenzenes, isomers of hexane, and so on conducted by several subsequent investigators gave an equilibrium temperature of 500-700° C and higher for different crude oils. Of course, these temperatures cannot be reached in sedimentary rocks. This circumstance was used by several investigators as proof of the high-temperature, plutonic origin of petroleum, which is incorrect. But the actual fact of the high-temperature ratios of several isomers in crude oils requires an explanation.

We assume that the pseudothermochemical character of radical reactions caused by energy transfer in the system solid phase-organic matter makes it possible to give this phenomenon a satisfactory explanation.

Several Analogies of Radiochemical and Radical Reactions /223

As early as 1924, S. Linde and D. Bardwell advanced the hypothesis that the radioactivity of rocks is possibly a factor promoting the transformation of organic matter into pe-roleum. This hypothesis came to currency, but soon interest in it waned, since it was definitely shown that the radiation in rocks summed together over even lengthy intervals of geologic time cannot have provided for the yield of hydrocarbons in the amounts actually observed in nature.

At the same time, based on the radiation hypothesis a successful explanation was found for several aspects of the petroleum formation process. This fact is of interest to us since in the mechanism of the action of ionizing radiation on organic matter and that of free radicals there is much that is common.

From the data of C. Sheppard and W. Barton, when fatty acids were irradiated with α-particles: caprylic ($C_7H_{15}COOH$), lauric ($C_{11}H_{23}COOH$), and palmitic ($C_{15}H_{31}COOH$), the gaseous irradiation products were found to contain 33-48 percent hydrogen, 34-51 percent carbon dioxide, 6-11 percent carbon monoxide, 0.4-0.7 percent methane, 0.6-1.0 percent ethane, 0.1-0.4 percent propane, and 0.2-0.8 percent butane. As the liquid products of the irradiation of lauric acid, n-undecane ($n\text{-}C_{11}H_{24}$) was identified, and as the irradiation product of palmitic acid -- n-pentadecane ($n\text{-}C_{15}H_{32}$). R. Hoenig studied the action of α-irradiation on several organic compounds, including hydrocarbons and bitumens. In all cases a large amount of hydrogen was observed to be given off, constituting 20-80 percent of the total yield of gases, along with several percent methane and its higher homologs. When compounds containing carboxylic groups were irradiated, the yield of CO_2 was sharply increased. For example, when dibasic sebacic acid ($C_8H_{16}COOHCOOH$) was irradiated, 68.9 percent carbon dioxide, 26.3 percent hydrogen, and 0.6 percent methane were given off, while the gaseous products of the irradiation of glycine (glycocol) -- NH_2CH_2COOH -- contained 55.8 percent CO_2, 19.0 percent H_2, 11.4 percent NH_3, and 4.8 percent CH_4.

Concerning the results of these experiments, it is essential to note that the reactions activated by radiation do not yield a complex mixture of products which would correspond to the random breaking of bonds at the site at which a high-energy particle collides with the molecule. This means that the particle energy is transmitted not at the bond, but at the molecule as a whole, while it cannot be uniformly distributed over all bonds. From steric considerations it follows that the action of the particle on the C-H bond is most probable and this bond is most often broken, which is indicated by the high yield of hydrogen in all experiments, regardless of the fact that the C-H bond energy is greater than the C-C bond energy. In other words, although the energy of activation is transmitted to the molecule as a whole, it is localized primarily at the terminal C-H bonds.

If the energy of excitation of the molecule were much smaller, /224 then obviously it could be transmitted further to the C-C bond and then, considering the lower C-C bond energy, one would expect the predominant formation of $CH_3^{\cdot}$ radicals instead of the H· radicals. This factor is significant in understanding the course of free radical reactions. The excitation energy of molecules when acted on by free radicals is lower than when acted on by high-energy particles, but higher than in ordinary reactions. In the latter, energy distribution by bonds is quite uniform, therefore it is not the terminal C-C bonds that are broken with the formation of weakly conjugated radicals of the $CH_3^{\cdot}$ type, but the scission of molecules into roughtly equal fragments. Accordingly, in mild cracking few gaseous products are always formed, including methane, but there is a predominance of gasoline-fraction hydrocarbons.

As for free radical reactions which are intermediate energetically between the usual and the radiochemical reactions, here the radical $CH_3^{\cdot}$ occupies a special place. This appears to us to be one of the reasons for the wide distribution of methane in the products of the catagenic transformation of organic matter, just as wide as one would expect for hydrogen if petroleum formation were caused by radiochemical processes.

Of high interest is the fact that irradiation leads to the intensive loss by molecules of functional groups, in particular, the decarboxylation of fatty acids, and the removal of amino groups and hydroxyl groups. The actual hydrocarbon structures do not undergo appreciable disruptions. The action of free radicals can be similar. Accordingly, the formation of hydrocarbons is not a process of their synthesis, but rather of their liberation from more complex organic compounds through cleavage of functional groups.

A third factor that should be noted in reference to experiments on the radiation conversion of organic matter is this: when fatty acids were irradiated with α-particles, hydrocarbons of normal structure were obtained. It was shown above, for example, that when lauric acid was irradiated, normal undecane was formed, but when palmitic acid was irradiated -- normal pentadecane. Recall that in experiments on the thermal catalytic conversion of fatty acids, hydrocarbons of iso-structure were produced, while hydrocarbons of normal structure always strongly predominate in crudes. C. Sheppard and W. Whitehead pointed out that at relatively low temperatures ketones are predominantly formed, and the decarboxylation reaction begins to predominate only with a considerable rise in temperature. Accordingly, they suggest that cleavage of molecules under the effect of high-

energy particles occurs as if in the heated state. In other words, these reactions can be viewed as pseudothermochemical caused by the conversion of the excitation energy of the irradiated molecules into vibrational energy. As was shown above, reactions of free radicals also can be viewed as "hot" reactions. /225

One of the oldest radiation-chemical reactions studied is the decomposition of water under the effect of α-particles. An important consequence of the radiolysis of water has been the action of this process on dissolved organic impurities. Even at a very considerable concentration of organic compounds, they decompose with the liberation of hydrogen, and sometimes also carbon dioxide, where nearly half the chemical activity produced in the water is transferred to the molecules of the solute (A. Allen, 1948).

It is believed that activated water consists of the free radicals $H^{\cdot}$ and $OH^{\cdot}$. No other kind of active particles in water could have had a long enough lifetime in order to successfully react with extremely dispersed molecules of the solute. Remarkably, the hydrogen yield in the radiolysis of water depends on the kind of irradiation. For irradiation with α-particles and deuterons, a high hydrogen yield is observed, while in x-ray irradiation little hydrogen is formed. A. Allen associated this fact with the concentration of radicals. Actually, electrons generated in water upon absorption of x-rays have the lowest density of energy release along their path (3 keV/cm) and yield the lowest concentrations of free radicals per unit volume. In contrast, α-particles (1430 keV/cm) and deuterons (175 keV/cm) intensively ionize over a short section and form a high concentration of radicals in a narrow zone located along the particle track. As a result, the probability is high that the radicals produced will recombine and thus, the stationary pressure of free hydrogen will also probably be high.

The appearance in water of the free radicals $H^{\cdot}$ and $OH^{\cdot}$ generated by the wall approaches in its consequences the process of radiation with a low density of energy release. Therefore the yield of active radicals is the highest, while the probability of recombination and formation of free hydrogen is extremely low.

In natural conditions, the solid surface of rocks is in contact with bound water, therefore the transfer of a free valency into the bulk and the activation of organic compounds most likely occurs through the intermediate formation of the radicals $H^{\cdot}$ and $OH^{\cdot}$. Here, due to the polarity of the $OH^{\cdot}$ radicals, the latter prove to be sorbed on the surfaces of solid particles, while the $H^{\cdot}$ radicals are transported into the bulk. This means that strongly-conjugated high-molecular radicals, upon breaking down at the surfaces, recombine with the $OH^{\cdot}$ radicals. As a

result, on the one hand, in the reacting system there accumulate compounds enriched in hydrogen, while on the other -- oxidized high-molecular compounds accumulate at the surfaces of the solid phase of rocks. /226

As we have seen, several facts of the chemistry of natural hydrocarbons explained by radiochemical processes, can be accounted for by the reactions of free radicals in the sense examined here that are close to the radiochemical processes, as to the nature of their action.

We have resorted to radiochemical reactions only in order to draw an analogy between them and radical reactions. However, in several cases they can be of independent significance. For example, it is nearly indisputable that deposits which are overlain with uranium ores owe their specific bituminosity to the radiation factor of the conversion of organic matter.

Several Geochemical Conclusions Following from the Proposed Model

The composition of petroleum in pools as well as the variation in its composition over the profile of sedimentary rocks not only depend on the particular mechanism of hydrocarbon formation, but are also determined by the nature of the initial organic material, the depth and nature of its alteration during its residence in the zone of diagenesis, processes of the transformation of petroleum (trace petroleum) in petroleum-parental rocks, and by the evolution of the composition of petroleum in pools, by the mechanism and stage (with respect to the development of the petroleum-formation process in petroleum-producing strata) of primary migration, by changes caused by secondary migration, by the complex of physicochemical conditions in crudes (including the mineral composition of the solid phase, the nature of stratal waters, and observation-reduction conditions), by the thermal and tectogenic history of the strata, and so on. However, many features of petroleum geochemistry doubtless are associated with the mechanism of the primary act of the initiation of hydrocarbons.

Governed by the model presented here, we can draw several conclusions concerning this aspect of the petroleum-forming process.

The question of the thermal regime of the petroleum forming process is invested with a new content.

Nearly all hypotheses of the origin of petroleum via chemical, including catalytic, transformation of organic matter consider heat

as an invariant factor of the petroleum-forming mechanism. The term "thermocatalytic" transformation has gained wide acceptance. Heat as a factor of the transformation of organic matter appears to be necessary from two points of view -- the thermodynamic and the kinetic: in the first place, owing to the low reserve of free energy in the organic compounds that are the initial compounds for crudes; and secondly, owing to the extremely low rate of organic reactions at low temperatures.

The above-considered principle of energy transfer in the conjugated system solid phase - organic matter makes it possible /227 to solve the problem of a deficiency of internal energy of organic compounds in endothermal reactions of hydrocarbon synthesis. As for the kinetics, then owing to the low energy of activation, the rate constant of radical reactions is much higher than the rate constant of any reactions of valency-saturated compounds. The limiting factor here is not the rate of the actual chemical reaction, but the intensity at which the radicals are initiated.

Since the process activated by free radicals is energetically equivalent to an increase in temperature in the system to 1000° C, in practice it is not essential whether it takes place in a medium at a temperature of 25 or 150° C.

The weak dependence of radical reactions on the temperature directly follows from the familiar differential relation for the rate constant k:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}.$$

Since the activation barrier of radical reactions is extremely low compared with ordinary reaction, the rate constant depends weakly on temperature. Hence it follows that the primordial petroleum (trace petroleum) formed in sedimentary rocks in a very broad range of temperature conditions must be a fairly monotypical substance.

The foregoing does not mean that temperature conditions do not in any control the process of petroleum formation. Here we are speaking only about the slight role of the thermal influence and the mechanism of the actual chemical reactions leading to the production of hydrocarbons. However, temperature is an essential parameter in the state of the solid phase. For example, the formation of structural defects of the Schottky defect type can be represented as the reaction in which atoms at a site dissociate into a vacancy and a free valency at the surface: $[V] + E_f =] + V$, where E_f is the energy of defect formation. The concentration of defects of this type is described by the expo-

nential function $n = c \exp(-E_f/kT)$, that is, the number of defects, and thus, the activity of rocks, to our understanding, increase with increase in temperature.

Moreover, as will be shown more closely in the next chapter, the broad development of radical reactions leading to the cleavage of hydrocarbons is possible when certain conditions are attained by the humified organic matter, which is also associated with the thermal history of the strata. Therefore temperature, or the generalizing parameters adopted by geologists that take temperature and time into account (geochronothermobath) of N. B. Vassoyevich and N. A. Kartsev, or the factor τ proposed by Lopatin /79/ to a large extent determine the intensity of the petroleum-forming process.

Many aspects of petroleum chemistry find a satisfactory explanation if we assume an intermediate stage of the existence of olefins, for example, the formation of alkanes of lower molecular structure from high-molecular aliphatic compounds, polymerization, and the formation of condensed structure. However, the formation of olefins is a highly endothermal reaction usually attained at temperatures beginning at 400-450° C. /228

In discussing the difficulties of explaining the origin of solid paraffin in crude oils, A. F. Dobryanskiy wrote: "The process would look quite differently if the transformation of petroleum had been accompanied by the influx of high-potential energy, for example, high temperature when the degradation of a long paraffin molecule into shorter fragments of normal structure in the form of methane and olefin hydrocarbons commences, followed by the hydrogenation of these olefins, however this necessitates temperatures that are so high as not to be admissible in crude oils from an oil deposit or find" /55, p. 70/.

The admissibility of the formation of olefins at a low ambient temperature is a remarkable feature of radical-conjugated reactions.

Actually, for example, the direct degradation of pentane into ethylene and propane at 25° C is thermodynamically forbidden:

$$C_5H_{12} \longrightarrow C_2H_4 + C_3H_8;$$
$$\Delta Z^0_{298} \quad (-1.9) \quad (-16.3) \quad (-5.6); \quad \Delta Z = +12.6 \text{ kcal/mole},$$

and only at 750° K does the ΔZ of the reaction correspond approximately to the equimolecular concentrations of these components:

$$C_5H_{12} \longrightarrow C_2H_4 + C_3H_8;$$
$$\Delta Z^0_{800} \ (+58{,}8) \quad (+24{,}5)(+30{,}5);\ \Delta Z = -4{,}3 \text{ kcal/mole}.$$

In the case of a radical-conjugated reaction, the similar process is thermodynamically quite feasible even at normal temperatures:

$$C_5H_{12} + H^{\cdot} \longrightarrow C_2H_4 + C_2H_6 + CH_3^{\cdot};$$
$$\Delta Z^0_{298} \ (-1{,}9)\ (+43{,}9)\ (+16{,}3)\ (-7{,}8)\ (+31{,}4);$$
$$\Delta Z = -2{,}1 \text{ kcal/mole}.$$

The pseudothermochemical character of free radical reactions means that "hot" reactions take place in a "cold" mass. Under thermal influence, the entire mass of the organic matter undergoes a successive series of chemical transformations. With the radical energy transfer, only the molecules that have been subjected to radical attack enter into chemical reaction. From this point of view obviously can be found the best explanation for the fact that in crudes profoundly transformed compounds coexist with compounds preserving nearly totally the structure /229 of the initial organic matter.

In accordance with this mechanism, H· radicals, in any case in part, derive from water. It should be noted that the isotopic composition of petroleum carbon differs somewhat from the isotopic composition of the hydrogen in organic matter, by being closer to the isotopic composition of water hydrogen.

The participation of water hydrogen in petroleum formation was suggested even by G. L. Stadnikov, who pointed to its deficiency in the organic matter that is primordial for petroleum. The idea that hydrocarbons were formed through the hydrogenation of organic matter found a detailed elaboration in work by V. A. Sokolov. Reactions activated by H· radicals formed on the wall approximate in their consequences the hydrogenation process, with, however, the difference that this process is carried out without the intermediate stage of hydrogen formation and is not a process of hydrogenation in the proper meaning of the word. Hence there is no need for any special sources of hydrogen (which are usually called the oxidation-reduction reactions of iron, radiolysis, and endogenic hydrogen), the need for which -- if one considers the absence of free hydrogen in sedimentary rocks -- is the weak point of the hydrogenation hypothesis.

The incorporation in petroleum hydrocarbons of water hydrogen during radical-conjugated reactions also improves the hydrogen

balance of the system, although the formation of petroleum predominantly through biochemical constituents rich in hydrogen, for example, lipids, does not actually make this problem in chemistry acute.

From the mechanism of the transformation of organic matter under the effect of radicals sporadically generated by the solid phase it follows that this process, to some extent, is discrete in nature. This feature of radical exchange reactions is capable of explaining the problem of petroleum geochemistry such as the absence in rocks of the products of intermediate stages of the transformation of organic matter into petroleum. Actually, if the process is conceived of as the successive modification of organic compounds, then obviously along with hydrocarbons intermediate compounds from the intermediate stages must be observed in the various sedimentary rocks. For example, as shown by experiments on the catalytic transformation of fatty acids, present in the catalysate along with the hydrocarbons is a considerable amount of ketones, including cyclopentanones and cyclohexanones. These compounds are not detected in the bitumenoids of sedimentary rocks.

The activity of the radical appearing in the system is localized at a single molecule, whose transformation is completed virtually in one stage. Chain reactions do not represent an exception, since they for the most part lead to the permanent reproduction of the same stage. As a result, the end products are obtained at once as if individual structures are "fired off," /230 including hydrocarbon structures, which in this way can be formed in the weakly altered mass of the remaining matter.

Associated with this is yet another geochemical feature of the action of this mechanism. In the rates of ordinary reactions, the limiting kinetics is the low kinetics of chemical transformations at low temperatures, therefore it is held that the formation of hydrocarbons is protracted in time. In the mechanism of radical exchange the frequency of the appearance of radicals is the limiting factor. In each such act of hydrocarbon formation, hydrocarbon molecules accumulate rapidly, but protracted in time. If during geologic time the sequence of stages of petroleum formation is differentiated, they must differ not so much by the qualitative composition of the matter (the so-called process of "maturing" of trace petroleum) as much as by the amount of hydrocarbons accumulated by the given instant. Of course, this situation characterizes only a tendency in the chemistry of hydrocarbon formation, since the metamorphism of organic matter in rock as a whole is determined by a set of factors.

These concepts are in good agreement with geologic data: if one cannot point out rocks in which compounds that are inter-

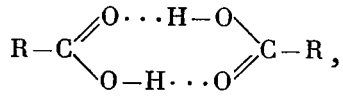
mediate with respect to hydrocarbons are present, one can point out a continuous series of petroleum-forming strata differing in the ratio of the amount of hydrocarbons to the total content of organic matter.

The process of petroleum formation in the conjugated system organic matter - solid phase assumes that the organic matter that was primordial for petroleum, as well as the hydrocarbon constituents formed are present in the diffused state, that is, exactly as is interpreted by the present theory of sedimentary-migratory origin of petroleum developed by N. B. Vassoyevich /7, 8/. Among other things, the term "trace petroleum" introduced by N. B. Vassoyevich exactly conveys the nature of the products formed through radical reactions. This is the literal sense of the work "trace", and as applied precisely to petroleum.

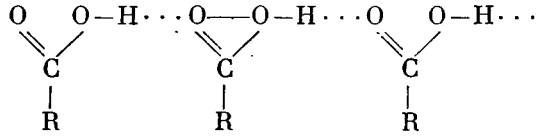
Radical reactions in which the radicals $H^{\cdot}$ and $CH_3^{\cdot}$ generated at the wall participate as the primary active particles cannot promote reactions of dehydrogenation. Predominant are the reactions culminating in bond rupture or double bond formation, followed by polymerization. Petroleum hydrocarbons must therefore be predominantly the products of these simple, single-stage reactions of the transformation of organic matter. The formation, let us say, of aromatic structures from saturated compounds requiring a multistage dehydrogenation process could hardly occur by the approach described, although in ordinary thermochemical reactions at temperatures corresponding to the necessary distribution of free energy levels, aromatic hydrocarbons can be obtained from any initial organic compound.

In accordance with the foregoing, the most applicable is /231
the concept of the predominantly inherited nature of the main hydrocarbon structures, namely the production of alkanes chiefly from aliphatic compounds, naphthenes -- from unsaturated fatty acids and other polyene lipids, and aromatic hydrocarbons -- -- from organic compounds containing aromatic rings (phenols, benzoic acids, aromatic amino acids, terpenes, and so on). Some cyclic constituents of the carotinoid /polyene/ type may have served as the initial compounds for the formation of hybrid naphthenic aromatic hydrocarbons. The significance of radical reactions in this sense in the first stage reduces to the liberation of these structures from the complexly structured organic compounds by bond rupture, removal of functional groups, and so on. Of course this does not mean that other processes of the transformation and synthesis of hydrocarbons did not take place at all. However, from the thermodynamic, kinetic, and isotopic points of view, the relationship between specific classes of petroleum hydrocarbons and specific biochemical constituents of the initial organic matter is wholly justified.

Since we have already referred to the possible role of hydrogen bonds, it is appropriate to note yet another factor. The more acidic the compounds, the stronger the hydrogen bonds they form with each other. Carboxylic acids, through the interaction of the carbonyl oxygen with the hydrogen atom of the hydroxyl group of another



form cyclic dimers, and the breaking of two hydrogen bonds of these products requires 13-14 kcal/mole. Besides the association leading to this dimeric cyclic species, there may also be the chain association:



Even more numerous are the possible associations between structural elements of proteins and carbohydrates containing amino, hydroxyl, and carbonyl groups.

Obviously, a high degree of association of humuslike compounds is due not only to the valency-saturated chemical bonds, but also to the hydrogen bonds.

In this respect it is important to note that hydrocarbons /232
do not form hydrogen bonds. When functional groups are lost, for instance, by fatty acids, or in some cases through the substitution of oxygen, nitrogen, or hydrogen, for example when a hydrogen in an alcohol is replaced with a methyl group (forming an ester), the possibility of hydrogen bonding is ended and the corresponding structures fall out of association. Because of this, hydrocarbon structures are virtually the only type of structures among biochemical constituents of organic matter that have the possibility of being segregated from humified matter.

The scheme of the transformation of organic matter in general outline has the following features. Interaction through the formation of hydrogen bonds of biochemical constituents of organic matter being degraded leads to the formation of strongly associated compounds of the humus type. By means of microbiological and chemical processes, gradually the functional groups

are removed in the form of the gaseous compounds: CO_2, NH_3, CH_4, and so on. At the same time the hydrogen bonds become fewer. As a result, on the one hand, there are more C-C bonds and a carbonaceous structure is formed, and on the other -- -- hydrocarbon structures are liberated and accumulate.

An increase in the content of low-polar lipids along with an overall decrease in the amount of unassociated lipids as the diagenesis of given sediments becomes more profound, observed by B. A. Romankevich and S. G. Batrakov [104] probably reflects exactly these tendencies.

A. Burlingheim et al. [124, 125], on analyzing kerogen from Green River shales, concluded that at least the peripheral part of the kerogen is formed by hydrocarbon type structures. M. Djuricic et al. [145] subjected this same kerogen to a more profound degradative treatment with a mixture of KOH and $KMnO_4$. As a result, more than 70 percent of the kerogen material was converted into unbranched aliphatic acids (C_8-C_{29}), saturated dibasic acids (C_4-C_{17}), isoprenoid acids with 2,6-dimethylpentane, 5,9-dimethyldecane, 2,6,10-trimethylundecane, 3,7,11-trimethyldodecane, 5,9,13,17-tetramethyloctadecane, and other structures, with small amounts of ketoacids and aromatic acids. These investigators suggest that the high yield of precisely these structures affords grounds to regard the corresponding structures as the main building blocks of kerogen, and not only of its peripheral part. In the model they suggest kerogen consists of "cores" linked by long aliphatic methylene bridges, and to the cores are attached unbranched and isoprenoid segments. The branching "points" are of some type that are sensitive to oxidative action or alkaline hydrolysis. It is wholly probable that these "points" are structures like those represented above, which were formed by functional groups associated through hydrogen /233 interaction. These structures are actually sensitive to the types of action mentioned. As we know, Green River shales yield petroleum hydrocarbons upon mild heating. Kerogen from these shales is a quite specific substance, chemically prepared for the generation or separation of hydrocarbons.

These considerations aim at underscoring that organic matter must in a certain way have been chemically prepared for the separation of hydrocarbons. We have avoided discussing the transformation of organic matter into hydrocarbons, since in our view the main structural groups of the future petroleum hydrocarbons, of both the methylene as aromatic types, are contained in the initial organic matter. Here our concern is only their liberation. Liberation takes place through dissociative

reactions and reactions in which olefin compounds participate, and the energetic aspect of these reactions is provided by a radical-conjugated mechanism. But for these reactions to actually lead to the segregation of hydrocarbons, the organic matter must be appreciably depleted of its active functional groups. Probably this chemical state of the matter is attained at the stage of its catagenesis corresponding to the long-flame or gaseous phase of the metamorphosis of bituminous coals, to which N. B. Vassoyevich /10, 64/ indicated as the beginning of the main phase of petroleum formation.

CHAPTER FIVE /234

ORGANIC MATTER IN CHLOROFORM-EXTRACTED BITUMENOID OF ROCKS

Correlations in the Change of Isotopic Composition of Carbon in Organic Matter and Bitumenoid in Sedimentary Deposits of the Russian Platform

Results of studying organic matter and bitumenoids makes it possible to compare the correlations of the distribution of the isotopic compositions of petroleum hydrocarbons over a profile and by area, and the correlations in the distribution of carbon isotopes in autochthonous organic material in rocks. The presence or existence of the corresponding correlations can afford grounds for evaluating the genetical relationship of crude oils with a given stratigraphic complex, the predominantly petroleum-generating role of particular deposits, and the scale, character, and direction of both local as well as regional migration.

In spite of several published works /23, 46, 65, 122, 126, 180, 197/, the isotopic composition of carbon in the organic matter of rocks (C_{org}) and bitumenoids (CB /chloroform-extracted bitumenoids/) has been studied to a much smaller extent and less systematically than the composition of carbon in petroleum and gas. It appeared useful to us before examining the details of the geochemical behavior of carbon isotopes in these materials to establish more general correlations. For this purpose, we undertook the analysis of the isotopic compositions of organic matter and bitumenoids from deposits of different geological age in the Russian Platform (E. M. Galimov, A. B. Ronov, and A. A. Migdisov, Doklad /Paper/, Volume 4, Vsesoyuznyy Simpoziume po Stabil'nym Izotopam /All-Union Symposium on Stable Isotopes/, /235 Moscow, 1972). To obtain representative statistics for data covering such an enormous territory necessitates hundreds and

thousands of determinations of carbon isotopic compositions for deposits in each geologic period. Of course, this is difficult because of technical limitations and time constraints, therefore for the rocks of each geologic age a so-called complex-mixed sample was compiled by mixing several hundreds of samples taken from different regions of the Russian Platform. And each sample was introduced into the mixed sample in the amount proportional to its content in the rock. The isotopic composition of the complex-mixed sample was analyzed in a spectrometer; the values thus obtained characterized the mean isotopic composition of the organic matter or the bitumenoid of the given geologic age (Fig. 55).

The following correlations were found:

1) the carbon of bitumenoid sampled on the average for the entire geologic profile is enriched in C^{12} relative to organic-matter carbon;

2) with change in the isotopic composition of carbon in organic matter, as a rule, there is a synchronous change, directed to the same side, in the isotopic composition of the carbon in chloroform-extracted bitumenoid;

3) change in the isotopic composition of C_{org} and CB across /236 the profile is not monotonic and therefore the variations in δC^{13} observed with geologic age are not controlled by the degree of metamorphism or by any other factors whose effect is proportional to the absolute geologic age; and

4) beginning with the upper proterozoic all the way to the Carboniferous, the isotopic composition of organic-matter carbon and bitumenoid-carbon are identical and correspond to the increased content of C^{12}.

A sharp enrichment in C^{13} occurred in the organic-matter carbon during the Carboniferous. Simultaneously, but to a lesser extent chloroform-extracted bitumenoid was enriched in the heavy isotope. Here, a difference of approximately 0.3 percent appeared between δC^{13} (C_{org}) and δC^{13} (CB), which difference persisted from this time throughout all subsequent geologic periods.

Total enrichment in the heavy carbon isotope of organic compounds during the Carboniferous can have been caused by various factors, for example, by an increase in the concentration of C^{13}

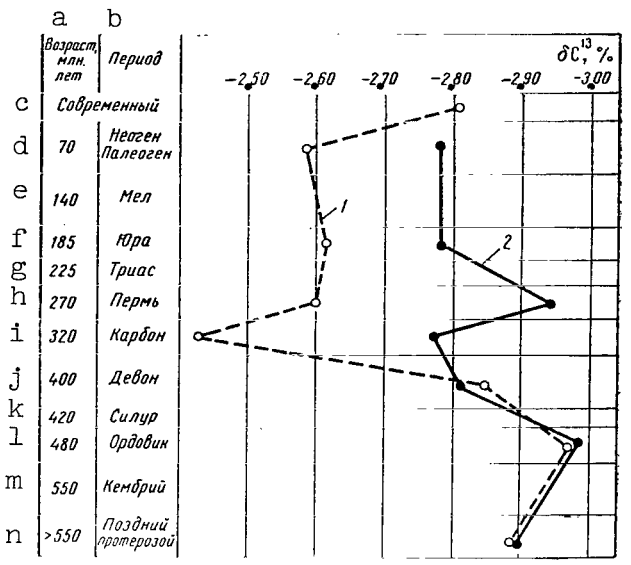


Fig. 55. Dependence of mean isotopic composition of carbon in organic matter (1) and chloroform-extracted bitumenoid (2) on geologic age of rocks in the Russian Platform

KEY:
a. Age, millions of years
b. Period
c. Recent
d. Neogene, Paleogene
e. Cretaceous
f. Jurassic
g. Triassic
h. Permian
i. Carboniferous
j. Devonian
k. Silurian
l. Ordovician
m. Cambrian
n. Late Proterozoic

during this period in the entire exchange stock through the incursion into the sedimentation basin of isotopically heavy carbon dioxide, by profound alterations in the biochemical structure of the organic matter developing during this period and subsequently persisting, and by the special facial character of the Carboniferous deposits in the Russian Platform.

During the Carboniferous there appeared a difference in the isotopic composition of C_{org} and in bitumenoids that had thus far been absent. Enrichment of bitumenoids in the light isotope indicates that they were formed from specific fractions of the structural groups of organic matter whose carbon was enriched in the light isotope while still present in the organic matter as such. Aliphatic and aromatic structures are among these isotopically light materials, as shown by a study of intramolecular isotopes effects. In the residual organic matter of rocks are concentrated heteroatomic compounds, whose carbon, in particular the carbon that is part of the functional groups, is enriched in the heavy isotope. In this respect, the absence of a notable difference in the isotopic compositions of C_{org} and CB in the Pre-Carboniferous Time possibly is accounted for by the weaker interconstituent differentiation of isotopes resulting from the more primitive organization of living matter.

Correlations of the Distribution of the Isotopic Composition of Organic Matter and the Chloroform-Extracted Bitumenoid Profilewise and Areawise in the Oil-Gas Province (Permian Ural Area) /237

Isolation of organic matter and chloroform-extracted bitumenoid from the investigated deposits of the Permian Ural Area as well as their quantitative determination and description were carried out by I. G. Kalachnikova. The results of the isotopic analysis are in Tables 53 and 54.

The most striking feature of the collection of rocks studied is the sharp enrichment in the heavy carbon isotopes of the organic matter from the Yasnopolyanian Substage. This involves /239 both the Tul'skoye and the Bobrikovskoye deposits.

TABLE 53. ISOTOPIC COMPOSITION OF CHLOROFORM-EXTRACTED BITUMEN FROM DEPOSITS OF THE PERMIAN URAL AREA

Deposit	Bore hole nr.	Stratigraphic complex	Sampling interval, m	Content in rock, wt. %		Intervening rock	CB·100 / C_{org}	δC^{13}, ‰
				C_{org}	CB			
Asyulskoye	31	C_2vr	1024—1099	0.625	1.25	Limestone		—2.86
Dubovogorskoye	2	C_2vr	1425—1430			Oil-bearing limestone		—2.75
Pavlovskoye	237	C_2vr	1302—1004	0.48	0.118	Sandstone	24.6	—2.91
Durinskoye	5	C_2vr	1913—1917	1.17	0.03	Limestone		—3.00
Berezniki	Ref.	C_2vr	1716—1718.8	0.37	1.25	»	>100	—2.89
Sivinskoye	1	C_2b	1310—1315.6	—	—	Oil-bearing limestone		—3.00
Durinskoye	3	C_2b	1933—1937	0.06	0.118	Limestone	>100	—2.97
Kasibskoye	1	C_2b	1487—1524	0.08	0.01	»	2.0	—2.99
Komarikhinskoye	351	C_2b	1697—1707	0.13	0.625	»	>100	—2.90
As above	351	$C_1oks+sp$	1899—1909.5	0.08	0.156	»	>100	—2.93
Kasibskoye	2	C_1tl	1742—1747		0.01	Aleurolite		—2.98
Dmitriyevskoye	5	C_1tl	1785—1790	1.51	0.04	»	2.6	—2.71
Golubyatskoye	101	C_1jsp	1905—1911	2.09	0.118	»	5.6	—2.60
Komarikhinskoye	1	C_1bb	1979.8—2009.4		0.2	»		—2.72
Sivinskoye	1	Wendian (Ishim)	2798.7—2802.2	0.63	1.25	Sandstone	>100	—3.18
»	1	Wendian (Arlan)	2836—2839	0.17	0.235	»	>100	—2.95

TABLE 54. ISOTOPIC COMPOSITION OF CARBON OF ORGANIC MATTER (C_{org}) FROM DEPOSITS OF THE PERMIAN URAL AREA /238

Area (deposit)	Borehole nr.	Stratigraphic complex	Interval m.	Content in rock, wt. % OM	Content in rock, wt. % CB	Intervening rock	$\beta = \frac{CB \cdot 100}{C_{org}}$	δC^{13}, ‰
1	2	3	4	5	6	7	8	9
Kuliginskaya	41	$C_1 jsp$	1667—1675	4.50	0.118	Aleurolite	2.6	—2.23
»	41	$C_1 ml$	1675—1682	4.80	0.08	Argillite	1.7	—2.32
»	41	$C_1 t$	1999—2006	0.57	0.118	Limestone	20.0	—2.60
Kuliginskaya	43	$C_1 jsp$	1635—1643	2.8	0.02	Argillite	0.7	—2.30
»	43	»	1643—1649	2.5	0.01	»	0.4	—2.35
»	43	$C_1 ml$	1694—1700	3.3	0.02	»	0.6	—2.68
»	43	$D_3 p$	2297—2300	0.8	0.02	»	2.4	—2.64
»	43	Rf	2365—2372	0.4	0.0006	Dolomite	0.14	—2.93
Tartinskoye	32	$C_2 ksh$	1066—1067	0.04	0.0025	Limestone	6.2	—2.24
»	32	$C_2 vr$	1137—1144	0.2	0.0012	Argillite	0.6	—2.47
»	32	$C_1 oks+sp$	1517—1524	0.9	0.04	Aleurolite	4.4	—2.99
»	32	»	1517—1524	1.7	0.04	Argillite	2.3	—2.98
»	32	$C_1 tl$	1524—1530	1.5	0.02	Aleurolite	1.3	—2.33
»	32	$C_1 tl$	1524—1530	1.6	0.005	Argillite	0.3	—2.30
»	32	$C_1 tl$	1557—1560	1.3	0.01	»	0.76	—2.39
»	32	$C_1 bb$	1574—1586	2.1	0.02	»	0.9	—2.20
»	32	»	1574—1586	3.6	0.04	Aleurolite	1.1	—2.17
»	32	$D_3 fr$	2039—2036	0.23	0.156	Dolomite	68.0	—2.93
»	32	$D_3 fr$	2235—2238	0.08	0.0025	Argillite	3.1	—2.80
»	32	$D_2 g$	2240—2246	0.5	0.04	Aleurolite	7.9	—2.58
»	32	$D_2 g$	2246—2252	0.5	0.02	Argillite	3.8	—2.54
»	32	V	2998—3001	0.3	0.0006	»	0.2	—2.75
Tazovskaya	3	$C_1 tl$	2059—2061	0.7	0.06	Aleurolite	9.2	—2.44
»	3	»	2071—2075	1.4	0.156	Argillite	11.4	—2.56
»	3	$C_1 bb$	2093—2098	1.4	0.156	Aleurolite	11.5	—2.29
»	3	»	2098—2100	0.52	0.118	»	32.7	—2.37
»	3	$D_3 kn$	2677—2680	0.34	0.08	Sandstone	22.8	—1.17
»	3	$D_3 kn$	2682—2684	0.34	0.06	Aleurolite	24.0	—2.49
Komarikhinskoye	351	$C_1 tl$	1943—1945	1.65	0.118	»	7.16	—2.27
»	351	»	1950—1951	1.65	0.156	»	9.45	—2.26
Durinskoye	5	$C_2 vr$	1909—1913	1.17	0.02	Limestone	1.71	—2.75
»	5	$C_1 oks+sp$	2205—2209	0.51	0.118	»	23.2	-2.73_3
»	5	$C_1 tl$	2252—2256	1.79	0.06	Argillite	3.35	-2.31_1
Sivinskoye	6	$C_2 vr$	1268—1272	0.37	0.0037	»	1.0	-2.50_0
Yumyshskoye	78	$C_2 b$	1541—1547	1.0	0.1	»	10	-2.89_9
»	78	$C_1 tl$	1795—1800	1.49	0.03	Limestone	2.08	-2.39_4
»	78	$C_1 tl$	1800—1804	1.65	0.02	Aleurolite	1.21	-2.40_1
Tukachevskoye	7	$C_2 vr$	1426—1431	0.27	0.0006	Limestone	0.22	-2.51_1
»	7	$C_1 tl$	1722—1725	1.0	0.02	Argillite	2.0	-2.77_0
Byrminskaya	301	$C_1 tl$	1793—1795	2.14	0.0025	»	0.11	-2.31_1
Morgunovskaya	53	$C_1 tl$	1938—1943	0.03	0.02	Limestone	66	-2.47_1

/ОМ = organic matter/

As was shown above, this enrichment of organic matter by heavy isotope in the Carboniferous is characteristic of the Russian Platform. Thus, we can conclude that this feature in the isotopic composition of C_{org} from the Yasnopolyanskiye deposits of the Permian Ural Area, part of the Russian Platform, is not associated with any local factors, but is caused by factors that are regional operative over all or nearly all the territory of the Russian Platform. At the same time, results of a more

detailed analysis conducted on material of a specific oil-gas province show that the isotopic composition of carbon in some ages of the Carboniferous Period was by no means identical (Fig. 56). In the Tournaisian the isotopic composition of organic matter is characterized by $\delta C^{13} = -2.60$ percent, while in the Yasnopolyanskiye deposits of the Visean Stage its mean isotopic composition is -2.38 percent, and the value of δC^{13} for the three investigated samples of C_{org} from the Oksko-Serpukhovskiye deposits of the Visean are -2.73 percent, -2.99 percent, and -2.98 percent, that is, they are considerably enriched in the light isotope. In the Kashirsko-Vereysko-Bashkirskiye deposits, the mean isotopic composition of C_{org} is expressed by the value -2.55 percent. However, overall for all the samples of the Carboniferous Age analyzed, the mean value of $\delta C^{13} = -2.46$ percent, very close to the value set on the average for the Carboniferous of the Russian Platform (-2.43 percent).

Organic matter in the Devonian deposits is isotopically lighter than in the Carboniferous deposits. This is also in complete agreement with the correlation established from average samples for the entire Russian Platform. But whereas for the terrigenic Devonian embracing the Kynovskiye and Pashiyskiye strata of the Franconian Stage, as well as the Zhivetskiy and Eifelian deposits, the isotopic composition of organic matter is expressed on the average by the value $\delta C^{13} = -2.56$ percent, in the carbonate Devonian is characterized by $\delta C^{13} = -2.87$ percent. The value of δC^{13} for C_{org} from the Wendian-Riphean deposits averages -2.84 percent, which indicates enrichment of the carbon by the light isotope, just as in the organic matter of the Upper Proterozoic deposits for the Russian Platform overall ($\delta C^{13} = -2.89$ percent).

There is no such well-defined correlation, obviously, in the distribution of the isotopic composition of the chloroform-extracted bitumenoid over the profile, above all because a relatively small number of deposits have been analyzed. In particular, there are no data for the Devonian and Tournaisian stages of the Carboniferous. Nonetheless, in the deposits which are characterized by enrichment of the organic matter in the heavy isotopes, a corresponding shift also in the isotopic composition of bitumenoid is observed.

Thus, the general pattern of variation in the isotopic composition of the carbon C_{org} and CB in the analyzed deposits of the Permian Ural Area agrees completely with the correlations established for the corresponding deposits of the Russian Platform as a whole.

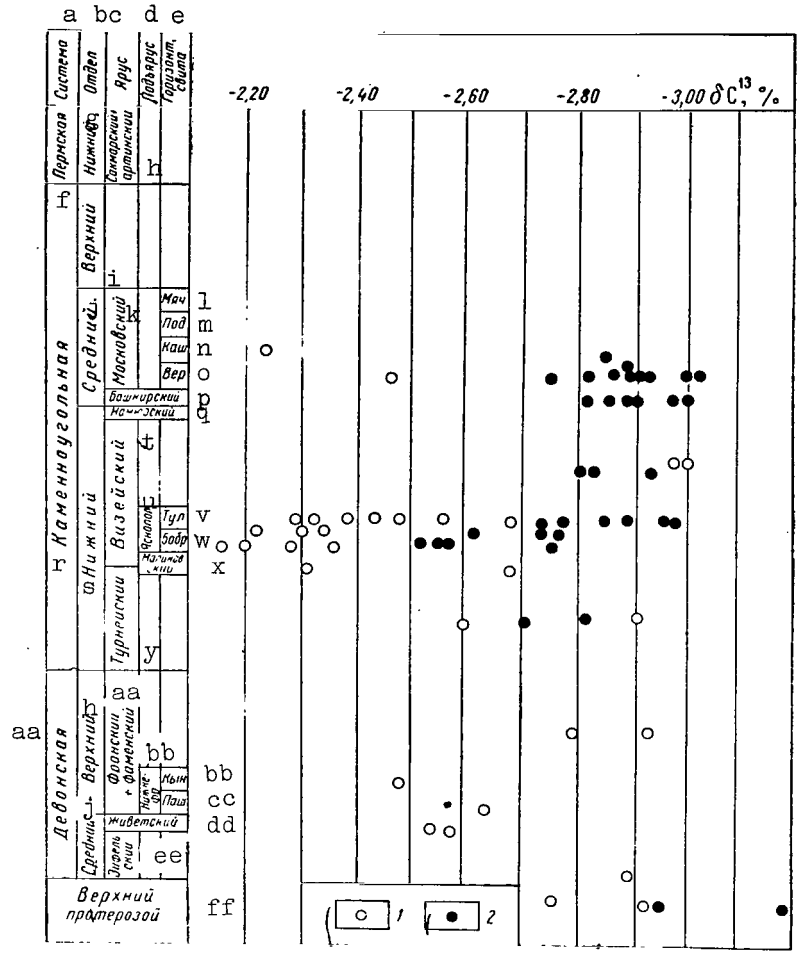


Fig. 56. Distribution of isotopic composition of carbon of organic matter (1) and chloroform-extracted bitumenoid (2) based on stratographic profiles of the Permian Ural Area.

KEY:
a. System
b. Division
c. Stage
d. Substage
e. Horizon, suite
f. Permian
g. Lower
h. Sakmarian-Artinian
i. Upper
j. Middle
k. Moscovian
l. Myach.
m. Pod.
n. Kash.
o. Ver.
p. Bashkirian
q. Namyurian
r. Carboniferous
s. Lower
t. Visean
u. Yasnolpolyanian
v. Tulian
w. Bobrinian
x. Malinovian
y. Tournaisian
z. Devonian

/Key continued on following page./

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aa. Franconian + Fammenean
bb. Kyn.
cc. Pash.
dd. Zhivetian
ee. Eifelian
ff. Upper Proterozoic

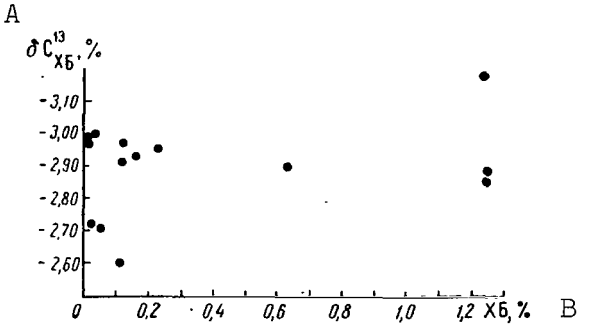

Fig. 57. Dependence of isotopic composition of carbon in chloroform-extracted bitumenoid on its percent content in rock
KEY: A. $\delta C^{13}_{СВ}$
B. СВ

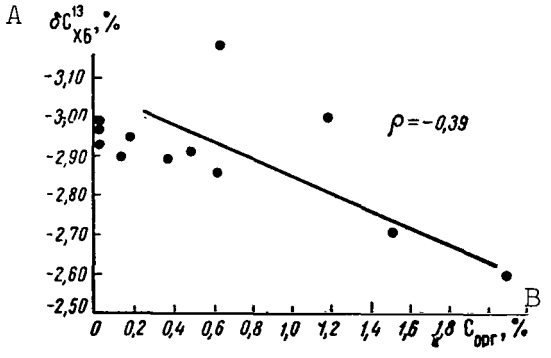

Fig. 58. Dependence of isotopic composition of carbon in chloroform-extracted bitumenoid on total content of organic matter in rock.
KEY: A. $\delta C^{13}_{СВ}$
B. C_{org}

No significant relationship was found between the isotopic composition of bitumenoid and its content in rock (Fig. 57). But there is a relationship, even though with a small coefficient of correlation ($\rho = -0.39$) between the isotopic composition of chloroform-extracted bitumenoid and the content of organic matter in rock: with decrease in the concentration C_{org} there is an increase in the light isotope content in bitumenoid carbon (Fig. 58). Approximately the same coefficient of correlation ($\rho = -0.36$) characterizes the dependence between the isotopic composition C_{org} and its content in rock (Fig. 59). Hence it follows that there must be a direct relationship between the isotopic compositions of bitumenoid and carbon in organic matter. /241

A comparison of the isotopic composition of organic matter from carbonate and sandy-argillaceous rocks of the same age shows that there is a tendency toward the relative enrichment of C_{org} from carbonates in the light isotope (Tables 55 and 56). In order to see how stable this tendency is, more determinations are needed. The cause of this

tendency can be the difference both in the nature of the organic matter entering the basin as well as the conditions of its accumulation and burial in carbonate and terrigenic sediments. A similar tendency is noted also for bitumenoids (Table 56).

We recall that similar comparisons for petroleum showed the absence of any dependence of its isotopic composition on the lithology of intervening deposits. /242

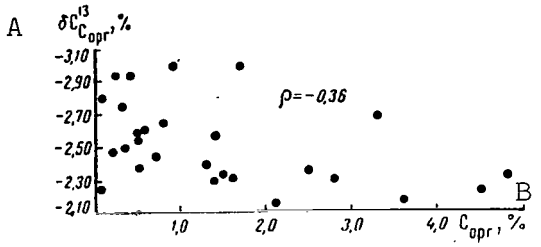

Fig. 59. Dependence of isotopic composition of carbon in organic matter on its content in rock.
KEY: A. δC^{13}_{org}
B. C_{org}

A comparison of the profile distribution of the isotopic composition of organic matter and petroleum at first glance leads to a wholly unexpected result. As noted above, Visean (Yasnopolyanskiye) crudes are among the lightest profile-wise, while the organic matter in the Yasnopolyanskiye strata is isotopically the heaviest. Here we do not have to speak of any process of inversion in the isotopic composition of the petroleum and the organic matter similar to the situation, for /243

TABLE 55. MEAN ISOTOPIC COMPOSITION OF CARBON IN ORGANIC MATTER FROM CARBONATE AND SANDY-ARGILLACEOUS ROCKS

Stratigraphic complex	Carbonates		Argillites, aleurolites	
	No. of samples	δC^{13}, %	No. of samples	δC^{13}, %
C_2vr+b	2	−2,59	20	−2,48
C_1jsp	2	−2,43	20	−2,36
C_1t	1	−2,60	—	—
D_3fm	1	−2,93	1	−2,80
$D_3fr+gv+ef$	—	—	4	−2,56
Rf	1	−2,93	1	−2,75

example, in which the formation and separation of isotopically light petroleum hydrocarbons leads to the enrichment of the organic matter in the heavier isotope. This is impossible from simple quantitative considerations. Moreover, the opposing character of the concentration of carbon isotopes by petroleum and by organic matter is not always observed. Thus, Bavlinskiye deposits contain isotopically light petroleum and isotopically light organic matter. In the carbonate Devonian of the Durinskaya Area petroleum extremely enriched in the light isotope (δC^{13} = = -2.98 percent) has been established. The carbon of C_{org} in these deposits is also enriched in the light isotope.

TABLE 56. MEAN ISOTOPIC COMPOSITION OF CARBON IN BITUMENOID FROM CARBONATE AND SANDY-ARGILLACEOUS ROCKS

Stratigraphic complex	Carbonates		Argillites, aleurolites	
	No. of samples	δC^{13}, %	No. of samples	δC^{13}, %
C_2vr+b	14	—2.90	2	—2.87
C_1isp	3	—2.91	9	—2.68
C_1t	2	—2.75	—	—
Rf	—	—	2	—3.06

Rather, the matter involves the following. Analyzed samples of C_{org} relate nearly exclusively to the Tul'sko-Bobrikovskiye deposits. Obviously, Yasnopolyanskaya petroleum is genetically unrelated to Tul'sko-Bobrikovskiye deposits. At the same time, at least for the northwest field, the individuality of the Yasnopolyanskiy type of petroleum and its distinction genetically from the lower lying Tournasian petroleum are indisputable. Evidently, the Malinovskiye deposits served as petroleum producing /244 deposits for Yasnopolyanskaya petroleum. The isotopic composition of C_{org} from the Malinovskiye deposits was measured only in a single sample from the Kuliginskoye Deposit that is in the southeast field. The measured δC^{13} value is -2.68 percent, that is, the carbonate is isotopically much lighter than the carbon of the C_{org} from the Tul'sko-Bobrikovskiye deposits.

The isotopic composition of C_{org} from the Tournasian deposits and the terrigenic Devonian in the Durinskaya Area is -2.60 and -2.64 percent, respectively. δC^{13} values characterizing the isotopic composition of the petroleum also correspond to the approximate equality of these values. The isotopic composition of the Tul'sko-Bobrikovskiye petroleum of the Kuliginskoye deposit is -2.78 percent, and that of the Devonian (Pashiyskaya) petroleum is -2.80 percent.

Owing to the segregation over this province of the northwest and southeast fields of the abundance of crude oils with different isotopic composition, it was of interest to find out whether there is a corresponding regionalization in the abundance of carbon isotopes of bitumenoids and organic matter (Figs. 60 and 61).

Correlations in the distribution of the isotopic composition of bitumenoids areawise suggest the conclusion that lower δC^{13} values correspond on the average to the northwest field than to the southeast field. True, these differences are not as distinctly expressed as for the crude oils. Whereas for the

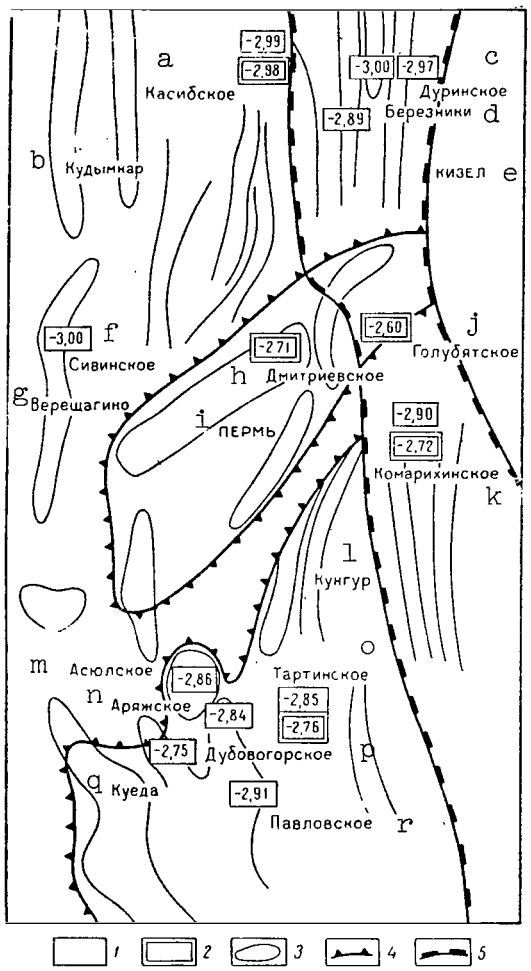

Fig. 60. Areawise distribution of δC^{13} values (in percent) characterizing the isotopic composition of carbon in chloroform-extracted bitumenoids (CB) from the Permian Ural Area

1. δC^{13} of the Middle Carboniferous deposits
2. δC^{13} of the Tul'sko-Bobrikovskiye deposits
3-5. Boundaries of tectonic elements of orders I and II, Kamsko-Kinel'skaya Depression and the Cis-Ural Trough

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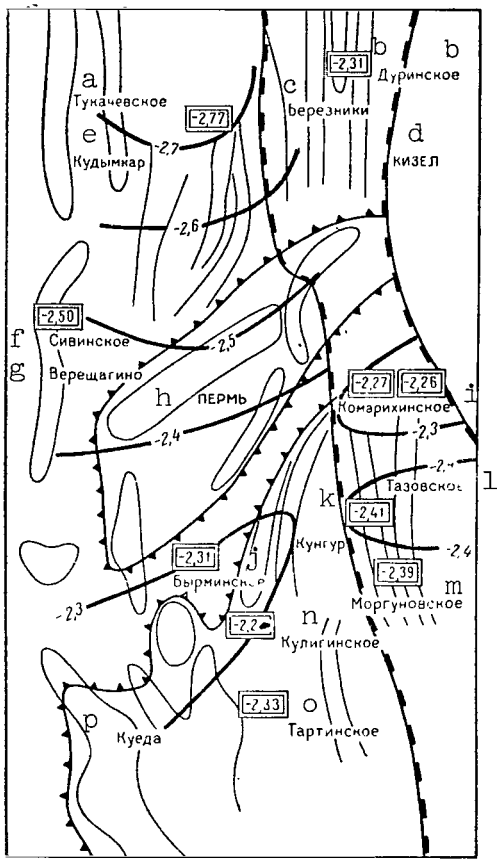

Fig. 61. Isolines of δC^{13} values (in percent) characterizing the distribution of the isotopic composition of carbon of organic matter (C_{org}) from the Tul'sko-Bobrikovskiye deposits of the Permian Ural Area

Symbols, see Fig. 60.

KEY: a. Tukachevskoye
b. Durinskoye
c. Berezniki
d. Kizel
e. Kud'imkar

/Key continued on following page./

/Key to Fig. 60 on preceding page./

KEY:
a. Kasibskoye
b. Kudymkar
c. Durinskoye
d. Berezniki
e. Kizel
f. Sivinskoye
g. Vereshchagino
h. Dmitriyevskoye
i. Perm'
j. Golubyatskoye
k. Komarikhinskoye
l. Kungur
m. Asyul'skoye
n. Aryazhskoye
o. Tartinskoye
p. Dubovogorskoye
q. Kuyeda
r. Pavlovskoye

/Key to Fig. 61 on preceding page -- continuation./

f. Sivinskoye
g. Vereshchagino
h. Perm'
i. Komarikhinskoye
j. Byrminskoye
k. Kungur
l. Tazovskoye
m. Morgunovskoye
n. Kuliginskoye
o. Tartinskoye
p. Kuyeda

crude oils we can take $\delta C^{13} = -2.87$ percent as the delimiting value, it turns out that in deposits of the northwest field there is not a single crude oil that is of heavier isotopic composition, and in the deposits of the southeast field -- not a single crude oil of lighter isotopic composition. As for the bitumenoids, we can speak only of the corresponding tendencies in the distribution of their isotopic composition areawise. Along with the relatively light bitumenoids in the areas of the northwest field, a bitumenoid with an isotopic composition of -2.71 percent has been established in the Dmitriyevskaya Area in the Tul'skiye deposits, and in the deposits of the southeast field -- the Pavlovskoye Deposit, the isotopic composition of the carbon from the bitumenoids sampled from the Vereyskiye deposits is characterized by $\delta C^{13} = -2.91$ percent. But on the average for the area the difference in the isotopic composition of the bitumenoids of the northwest and southeast fields is quite substantial, -2.93 and -2.78 percent, respectively (Table 57). /245

It is extremely revealing that the mean isotopic compositions of crude oils and bitumenoids relating to the same stratographic complex practically coincide: over the areas of the southwest field the δC^{13} of the crude on the average is -2.92 percent, and for bitumenoid -- -2.93 percent; in the areas of the southeast field the values are -2.80 and 2.78 percent, respectively.

In several cases there are data on the isotopic composition of the carbon in petroleum and chloroform-extracted bitumenoid

TABLE 57. COMPARISON OF ISOTOPIC COMPOSITION OF CHLOROFORM-EXTRACTED BITUMENOIDS OF THE MIDDLE CARBONIFEROUS-VISEAN DEPOSITS OF THE NORTHWEST AND SOUTHEAST FIELDS OF THE PERMIAN URAL AREA

Northwest Field			Southeast Field		
Area	Age	δC^{13}, %	Area	Age	δC^{13}, %
Sivinskaya	C_2vr	—3.00	Dubovogorskaya	C_2vr	—2.75
Durinskaya	C_2vr	—3.00	Pavlovskaya	C_2vr	—2.91
Berezniki	C_2vr	—2.89	Komarikhinskaya	C_2b	—2.90
Asyulskaya	C_2vr	—2.86	Golubyatskaya	C_1jsp	—2.60
Kasibskaya	C_2b	—2.99	Komarikhinskaya	C_1jsp	—2.72
Durinskaya	C_2b	—2.97	Tartinskaya	C_2vr	—2.76
Dmitriyevskaya	C_1jsp	—2.71	Aryazhskaya	C_2vr	—2.82
Kasibskaya	C_1jsp	—2.98			
δC^{13}_{av} of bitumenoids		—2.93			—2.78
δC^{13}_{av} of petroleum		—2.92			—2.80

relating to the same stratographic complex of the same deposit. A comparison of these data (Fig. 62) shows that there is a direct relationship between them, with a fairly high coefficient of correlation ($\rho = 0.81$). If by resorting to additional analytical methods it is possible to firmly establish the syngeneticity of these bitumens, this relationship can be of serious significance for arguing the genetical confinement of crude oils to deposits of the corresponding stratographic complexes. Further analyses in this direction are needed. /246

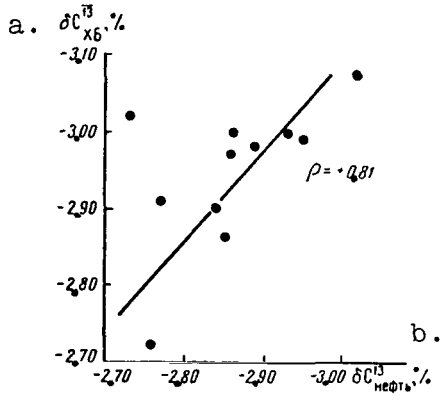

Fig. 62. Relationship of isotopic composition of carbon in chloroform-extracted bitumenoids and petroleum from like deposits of the same areas in the Permian Ural Area

KEY: a. $\delta C^{13}_{\text{CB}}$

b. $\delta C^{13}_{\text{petroleum}}$

It should be noted that correlations involving the isotopic composition of organic matter or bitumenoids unquestionably must be less clearly defined than correlations relating to the isotopic composition of crudes. Petroleum, being a mobile substance, has a much more homogenized, averaged isotopic composition, representatively characterizing the given pool, the given horizon. Study of the isotopic composition of organic matter characteristic of a given horizon from the results of analyzing individual samples carries considerably greater danger of obtaining

random values of δC^{13} uncharacteristic on the average for the given deposits. Here considerably more stratigraphic material is needed for a confident interpretation.

CHAPTER SIX /247

GASES OF SEDIMENTARY ROCKS

Distribution of Carbon Isotopes in Gases

Background

Natural gas is enriched in C^{12} relative to the carbon in petroleum and organic matter and is characterized by a much broader range of variation in isotopic composition.

A comparison of gases present in rocks in different states, that is, by-product petroleum gases, and gases that are free or dissolved in water shows that their isotopic composition varies approximately within the same limits. Among petroleum gases is found methane, both isotopically heavier (δC^{13} = -3.5 percent) as well as considerably enriched in the light isotope. Thus, for example, are the gases of the petroleum deposits Ken-Kiyak (δC^{13} = -5.62 percent) and especially Akzhar (with δC^{13} from -5.02 to -6.48 percent). In the by-product gases of several petroleum products we analyzed from the Volgo-Uralskaya Oil-Gas Province, the isotopic composition of methane varied from -3.63 to -5.72 percent. An equally broad range of variation in δC^{13} is characteristic of free and water-dissolved gases (Fig. 53).

The considerable amount of methane present in the sedimentary deposits is associated with the Carboniferous deposits. This methane is given off during metamorphosis (catagenesis) of bituminous coals and is present both in the free as well as in the adsorbed state in the pore space of coals.

Analysis of the isotopic composition of methane associated /248
with the coals of the Vorkuta Basin showed that its isotopic composition does not differ appreciably from that of the methane of hydrocarbon gases from petroleum deposits and gases diffused

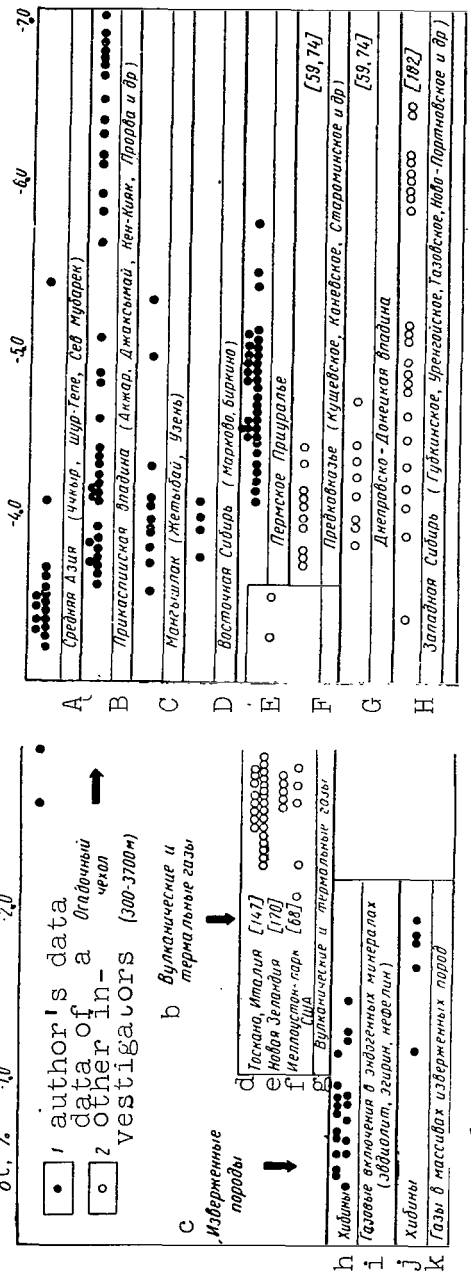

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Fig. 63. Isotopic composition of methane carbon from several regions of the USSR (data for volcanic and thermal gases -- for foreign areas)

in sedimentary rocks. The mean $\delta C^{13} = -4.43$ percent is close to the $\delta C^{13}_{av} = -4.44$ percent corresponding to the isotopic composition of hydrocarbon gases lying in the same range of depths, that is, 500-1000 m (Table 58). However, isotopically heavier gases are also encountered, associated with coals of high degrees of metamorphism /222/. Relatively isotopically heavy gases are characteristic of deposits of the Amu'-Dar'ye Syneclise (Uchkyr -- δC^{13} from -3.27 to -3.64 percent; Saman-Tepe -- δC^{13} from -3.28 to -3.44 percent; Koyun -- $\delta C^{13} = -3.21$ percent; Keli -- $\delta C^{13} = -3.50$ percent; Sharapli -- $\delta C^{13} = -3.28$ percent; Yelanskoye -- $\delta C^{13} = -3.48$ percent; Geslimskoye -- $\delta C^{13} = -3.31$ percent, and so on). The pools analyzed, pertaining to complexes of the Carbonate and Terrigenic Jurassic, were buried here at 1700-2800 m. The isotopically heaviest gas ($\delta C^{13} = -2.64$ percent) is found in the Guardakskaya salt-bearing strata (J_3km + t) at a depth of 3500 m. /249

Below we will consider in detail the possible mechanisms of the fractionation of carbon isotopes in gases and on this basis indicate the more intimate relationships between the isotopic composition and the origin of gas. Here, in contrast, it is desirable to stress the commonality of gases in sedimentary rocks, which is that they are substantially, although in different degrees, enriched in C^{12} relative to organic matter (Fig. 64) and in this sense differ sharply, for example, from volcanic gases and gases in igneous rocks (the latter are examined in a separate section).

/KEY to Fig. 63/

a. Sedimentary cover (300-3700 m)
b. Volcanic and thermal gases
c. Igneous rocks
d. Toscana, Italy
e. New Zealand
f. Yellowstone Park, US
g. Volcanic and thermal gases
h. Khibiny Range
i. Gas inclusions in endogenic minerals (eudiolite, aegirite, nepheline)
j. Khibiny Range
k. Gases in massifs of igneous rocks
A. Central Asia (Uchkyr, Shur-Tepe, No. Mubarek)
B. Caspian Basin (Akzhar, Dzhaksymay, Ken-Kiyak, Prorva and others)
C. Mangyshlak (Zhetybay and Uzen')
D. Eastern Siberia (Markovo and Birkina)
E. Permian Ural Area
F. Cis-Caucasus (Kushchevskoye, Kanevskoye, Starominskoye, and others)
G. Dneprovsko-Donetskaya Basin
H. Western Siberia (Gubkhinskoye, Urengoyskoye, Tazovskoye, Novo-Portnovskoye, and others)

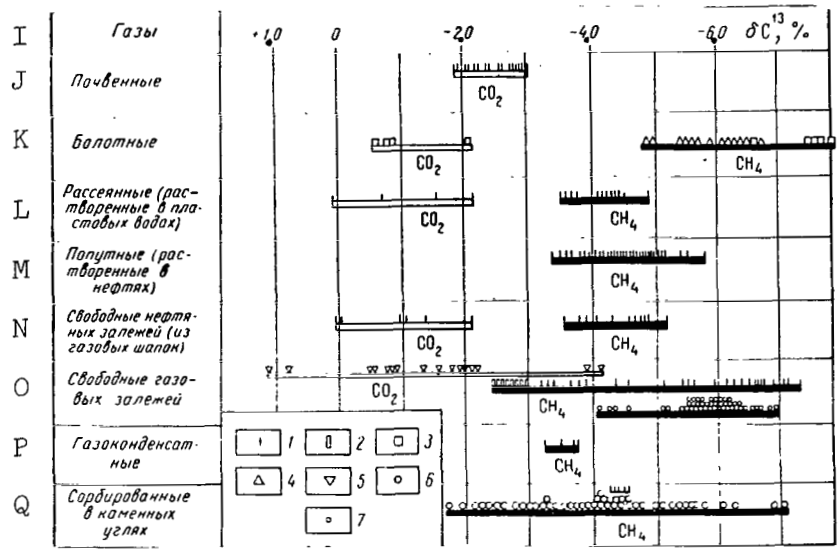


Fig. 64. Isotopic composition of carbon in CO_2 and CH_4 in gases of different morphology

Data from different investigators: 1. Author's; 2. V. Stahl /222/; 3. S. Oana and E. Deevay /203/; 4. V. L. Lebedeva et al. /60, 74, 80/; 5. R. Zartman et al. /235/: 6. U. Colombo, F. Gazzarrini et al. /129/; 7. U. Colombo, R. Teichmuller et al. /128, 139/.

/KEY on following page/

/Key to Fig. 64 on preceding page -- continuation./

I. Gas
J. Soil
K. Swamp
L. Diffused (dissolved in stratal water)
M. By-product (dissolved in petroleum)
N. Free, in petroleum pools (from gas caps)
O. Free, from gas pools
P. Gas-condensate
Q. Sorbed in bitumenous coals

Variation in Isotopic Composition of Methane Across Sedimentary Rock Profile /250

As was indicated by the author in several studies /35, 151, 152/, there is a regular variation in the isotopic composition of methane across a geologic profile. With increase in bedding depth of rocks, there is an increased content of the heavy isotope therein.

In juvenile, shallow-buried deposits, methane of very light isotopic composition is often encountered -- just as in swamp gases. A typical deposit of this type is the methane pool we analyzed in the Paleogenic deposits of the Akkulovsko-Bazayskaya Area of the Northern Ural Area. The hydrocarbon fraction of the gas here is represented nearly entirely by methane, whose isotopic composition is characterized by δC^{13} values from -6.36 to -7.21 percent. The bedding depth of the productive horizon is about 330 m. Earlier, gas deposits containing methane having this isotopic composition were described by N. Nakai /200/ in Japan and by U. Colombo /127/ in Southern Italy and Sicily.

It should be noted that pools of methane anomalously enriched in the light isotope are a not infrequent phenomenon, caused by the distinctiveness of the specific geochemical environment; they are characteristic in general of the upper layer of sedimentary rocks. G. Wasserburg, E. Mazor, and R. Zartman /230/ observed methane enriched with the light isotope, with δC^{13} from -5.09 to -8.44 percent, in the surface (40-100 m) deposited (drift) strata of the Glacial Period.

In addition to the above-noted Akkulovsko-Bazayskaya Area, gas of extremely light isotopic composition was established in /251
the Cretaceous deposits Akzhar (δC^{13} = -6.48 percent) and in the Jurassic, Ken-Kiyaka (δC^{13} = -5.80 percent), while deeper-lying gases of the same deposits are characterized by higher values (Fig. 65).

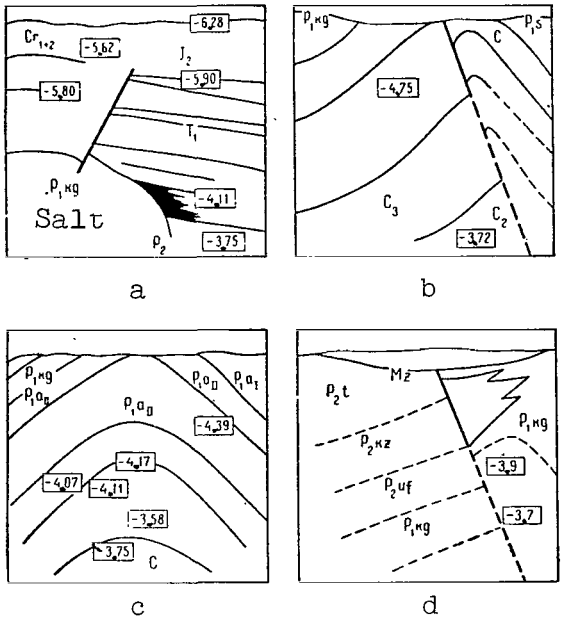


Fig. 65. Distribution of $\delta C^{13}_{CH_4}$ (in percent) across the profile of several areas in the Caspian Area
a. Kenkiyakskaya
b. Aleksandrovskaya
c. Zhilyanskaya
d. Dzhusinskaya

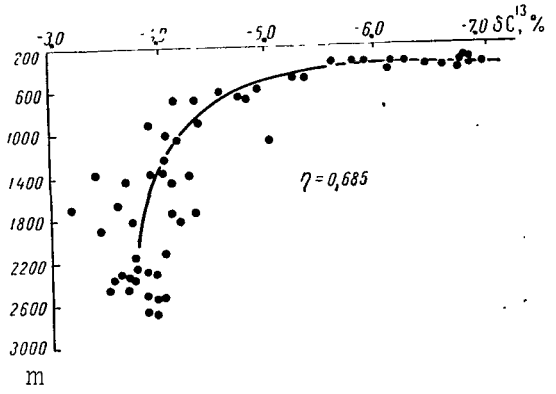


Fig. 66. Dependence of isotopic composition of carbon in methane on its bedding depth (η = coefficient of correlation)

Fig. 66, plotted from the results of an analysis of gases mainly from the Caspian Depression, illustrated this tendency. By using the data of R. Zartman et al. [23], we found that this tendency is also characteristic of gases from North American deposits (Table 58).

TABLE 58

Interval of bedding, m	North America		Caspian Depression	
	No. of samples	δC^{13}_{av}, ‰	No. of samples	δC^{13}_{av}, ‰
0—500	2	—4,84	18	—6,38
500—1000	13	—4,29	9	—4,44
1000—1500	7	—4,02	10	—4,08
1500—2000	7	—3,79	7	—3,78
2000—2500	3	—3,52	12	—3,60
2500	5	—4,25	4	—4,26

In Fig. 67, we produced from a study by W. Sackett [21], there are summarized the results of an analysis of the isotopic composition of methane obtained by several foreign investigators. The data in the graph is represented as a function of the geologic age of the intervening deposits. Some investigators subdivided

gases by the isotopic composition of carbon into Cenozoic, Mesozoic, and Paleozoic /59, 60/. But, as can be seen from Fig. 67, the mean isotopic composition and limits of the variation in δC^{13} characterizing the isotopic composition of gases from the Cambrian to the Mesozoic, that is, over an extent of about 500 million years, do not depend on the deposit age. Only gases from the Pliocene and Quaternary deposits as a rule, buried shallowly, are notably enriched in the light isotope.

/252

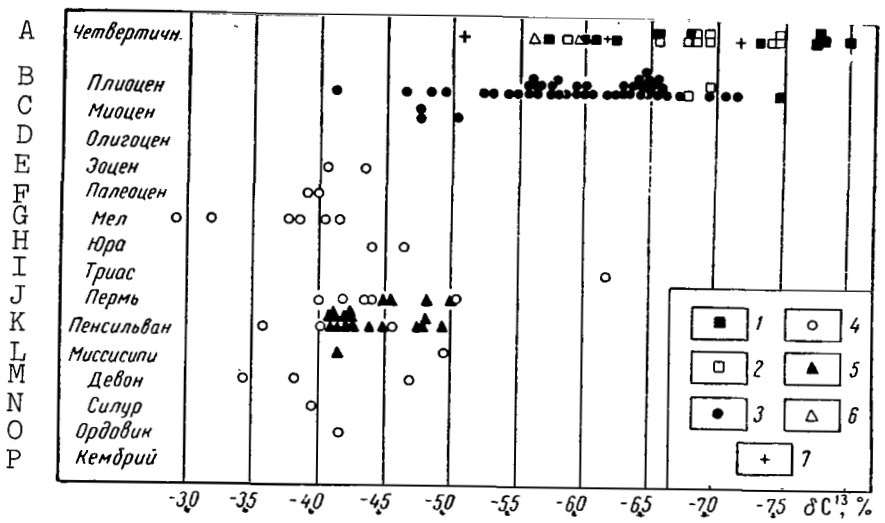


Fig. 67. Isotopic composition of carbon in methane from the data of foreign investigators. Reproduced from a study by W. Sackett /215/
1. S. Oana and E. Deevay /203/; 2. N. Nakai /200/; 3. U. Colombo et al. /127/; 4. R. Zartman et al. /235/; 5. G. Newton and W. Sackett /203/; 6. Unpublished data of W. Sackett and Emery; 7. G. Wasserburg et al. /230/

KEY:
A. Quaternary
B. Pliocene
C. Miocene
D. Oligocene
E. Eocene
F. Paleocene
G. Cretaceous
H. Jurassic
I. Triassic
J. Permian
K. Pennsylvanian
L. Mississippian
M. Devonian
N. Silurian
O. Ordovician
P. Cambrian

The fact that the variation in the isotopic composition of a gas across the profile of sedimentary deposits is determined more by the bedding depth than by the age of the deposits is

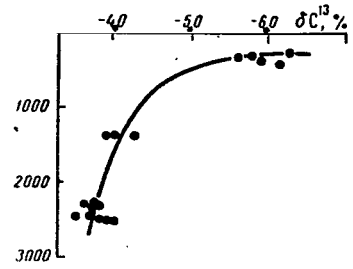


Fig. 68. Dependence of isotopic composition of carbon in same-age (Jurassic) gases on their bedding depth.

illustrated by Fig. 68. The δC^{13} values characterizing methane gas from single-age (Jurassic) deposits of the Caspian depression and Mangyshlak (the deposits Akzhar, Prorva, Zhetybay, Uzen', and Ken-Kiyak) vary over a broad range, from -3.81 to -6.58 percent. Here the same dependence of the isotopic composition of methane on depth is observed as was shown in Fig. 66.

Of interest are the results of an analysis of the isotopic composition of gases from ancient deposits elevated or exposed at the present time at the surface. Thus, the isotopic composition of carbon in methane from square 491a within the Voronezhskiy prominence (area of Peski), where at a depth of about 300 m an influx of rocks of crystalline foundation was obtained, is -6.21 percent, typical of surface rocks. Gas from the Upper Proterozoic deposits of the Pechengskiy Rayon of the Kola Peninsula, sampled at a depth of 100 m, proved to be enriched in the light isotope, δC^{13} = -6.0 percent (both the samples were presented by I. A. Petersil'ye). Therefore, in ancient rocks lying near the surface isotopically light methane is generated, characteristic of juvenile deposits, more exactly, characteristic of the upper zone of sedimentary rocks. In the more deeply buried ancient deposits isotopically heavier methane is correspondingly observed. For example, gas from the Archaen rocks of the crystalline foundation of the Russian Platform (Kaluzhskaya Oblast, Yakshunovskaya Area, square 12) from a depth of 900 m has δC^{13} = -4.33 percent, with the following composition: CH_4 -- 7.13 percent, CO_2 -- 1.71 percent, residual nitrogen, argon, and helium. This value corresponds to the mean isotopic composition of carbon in methane gases at the same depth as for the sedimentary rocks of the Phanerozoic. /253

A hypothesis was advanced that the gradient in the isotopic composition of gases with depth is due to the temperature gradient, since the kinetic isotopic effect of the gas formation depends on temperature /28/. A similar point of view as to the nature of the isotope effects in gases was given by W. Sackett: "...isotopic data show that with increase in temperature and in age of methane pools there is a smaller difference in the isotopic composition of methane and of the original material in rocks. Since in a sedimentary basin both temperature and age increase with depth, the δC^{13} values of the pools of natural methane must become more positive with increase in depth of the reservoir given the condition that the organic material of the parent rocks has the same isotopic composition" /215, p. 855/.

In the following sections we examine in more detail the mechanism of the formation of the isotopic composition of gas. In these sections it will be shown that the kinetic isotope effect as generally understood is not the only, and evidently, far from the principal factor in the isotope fractionation occurring in gases. However, it is essential that regardless of the causes for this phenomenon, the isotopic composition of methane discloses a relationship with the Recent hypsometric position of intervening rocks. Accordingly, of no less significance is the conclusion advanced earlier /28/ on this basis, that gases observed today in deposits of any geologic age were formed not long ago, on the average during a time that is shorter than would be necessary for a substantial variation in the geologic structure of the sedimentary complex (variations in Recent depths of bedding of stratographic horizons). Gases of more ancient age evidently are older than the Paleogenic, for the most part having been diffused.

Ethane, Propane, and Butane in Free and By-Product Petroleum Gases /254

The isotopic composition of carbon in heavy homologs of methane in gases has been analyzed most fully by U. Colombo, R. Gazzarrini et al. /127/; they measured the δC^{13} of individual hydrocarbons from methan to butane inclusively, from Neogene-Paleogene gas pools of Northern Italy (Table 59). From their data, in the series CH_4—C_2H_6—C_3H_8—C_4H_{10} each successively higher homolog is enriched in C^{13} compared with the preceding member of this series, where this relationship is observed in all samples without exception.

The difference of our investigation is that we studied not free gases, but gases dissolved in petroleum /43/. This distinction can prove to be substantial, since generally speaking the thermodynamics of free gases in gas deposits and by-product gases in petroleum deposits differs: in the first case the hydrocarbon system is restricted to the first members of the methane series up to butane, inclusively, and in the second case it includes the entire set of petroleum hydrocarbons.

We should also say something about the method of sampling, since in the case when gaseous compounds are analyzed it can strongly affect the end result. The samples were taken by means of hermetic stratal samplers immediately across from the perforation interval. As a result, the petroleum-containing dissolved gas enter the laboratory having been in conditions of stratal pressure, without the loss of any constituents. In addition, we believed it important in studying the ratio of isotopes in different individual hydrocarbons to sample only in newly discovered deposits where the stratal pressure was not reduced through exploi-

TABLE 59. ISOTOPIC COMPOSITION OF HYDROCARBON CONSTITUENTS OF GAS DEPOSITS IN ITALY /127/

Age of rock	Depth, m	δC^{13}, %			
		CH_4	C_2H_6	C_3H_8	C_4H_{10}
Miocene	1552	−4.77	−3.05	−2.65	−2.34
Pliocene	1476	−5.76	−3.22	−2.64	−2.27
»	1558	−5.95	−3.31	−2.70	−2.53
»	1636	−5.76	−3.25	−2.57	—
»	1957	−5.29	−3.23	−2.53	—
»	1906	−4.64	−3.19	−2.52	−2.28
»	1585	−4.84	−2.96	−2.53	−2.26

tation and, therefore, the phase ratios of the petroleum hydrocarbons and the dissolved gas wholly corresponded to the natural ratios. This was possible only through close cooperation with the Permneft' Association and the Kama Branch of the All-Union Scientific Research Geological-Prospecting Petroleum Institute (A. Z. Koblova, N. A. Nakoryakova, N. A. P'yankov, and V. I. Posyagin). /255

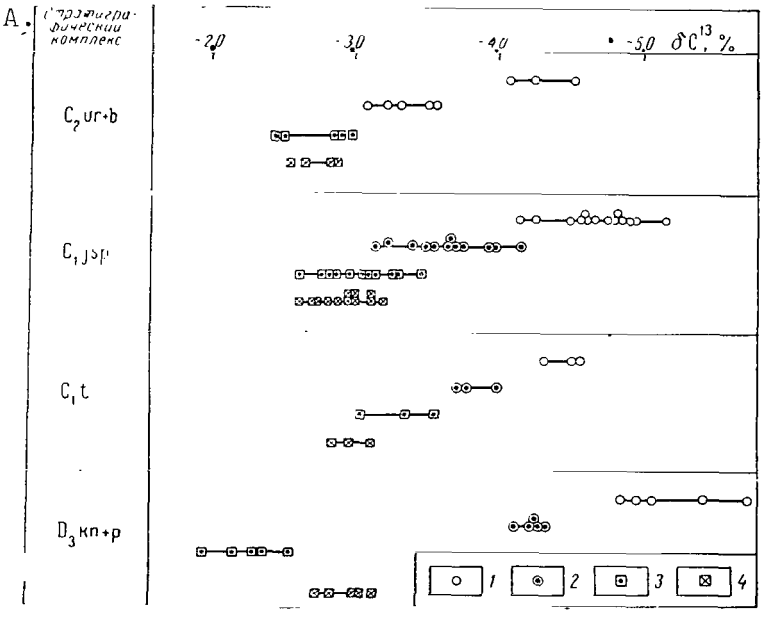


Fig. 69. Mean δC^{13} values for pools analyzed, characterizing the isotopic composition of carbon in individual hydrocarbon constituents from the main productive horizons of deposits in the Permian Ural Area
1. CH_4; 2. C_2H_6; 3. C_3H_3; 4. C_4H_{10}
KEY: A. Stratographic complex

The distribution of carbon isotopes in the gases studied is characterized by the following general features (Fig. 69). The isotopically lightest constituent is methane (δC^{13}_{av} = 4.70 percent); in the higher homologs light isotope enrichment is reduced; ethane has δC^{13}_{av} = -3.71 percent, propane δC^{13}_{av} = -2.90 percent, and butane δC^{13}_{av} = -2.88 percent. Thus, just as in free gases, in the by-product gases we analyzed there is a depletion of the C^{12} carbon isotope with increase in the molecular weight of hydrocarbons. With increase in the molecular weight, there is also a smaller difference between the isotopic composition of a neighboring pair of hydrocarbons. It was found that along with samples that have this "normal" distribution of isotopes, there exist samples with anomalous isotope distribution. The anomaly is that, first of all, they contain propane and butane that are enriched in the heavy carbon isotope compared with petroleum overall, and secondly, propane in these gases is the heaviest constituent -- it is isotopically heavier than butane, that is, there is an inversion in the isotopic shifts. /256

Fig. 70 compares the isotopic compositions of carbon in individual hydrocarbons. There is no relationship between the isotopic composition of methane and the isotopic composition of the heavier hydrocarbons. But between the isotopic compositions of ethane, propane, and butane a quite satisfactory correlation has been noted. For the pair C_2H_6—C_3H_8, the coefficient of correlation is + 0.75, and for the pairs C_2H_6—C_4H_{10} and C_3H_8—C_4H_{10} it is + 0.64 and + 0.62, respectively.

A substantial difference was detected in the δC^{13} values of the gas constituents and also in the nature of the variation of these quantities from methane to its homologs, for gases from different productive horizons. In Permskaya Oblast the Yasnopolyanskiye deposits of the Lower Carboniferous and the terrigenic Devonian are regionally petroleum-bearing. Oil pools are also encountered in the Middle Carboniferous and in the Tournasian. /257

As we can see from Fig. 69, characteristic of gases from the Yasnopolyanskiye and Middle Carboniferous deposits is an increased content in the light carbon isotope, from methane to the higher homolog. Here the carbon of each of the gas constituents from the Middle Carboniferous deposits is heavier (by approximately 0.4 percent) than the corresponding constituent in the Yasnopolyanskiye gases.

The above-noted "anomalous" distribution of carbon isotopes in individual hydrocarbons is characteristic for nearly all

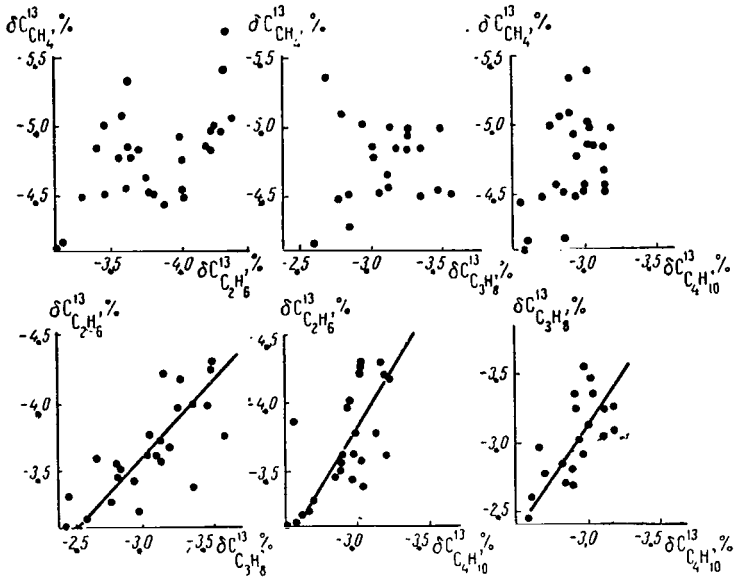


Fig. 70. Relationship between values of individual hydrocarbons in by-product petroleum gases.

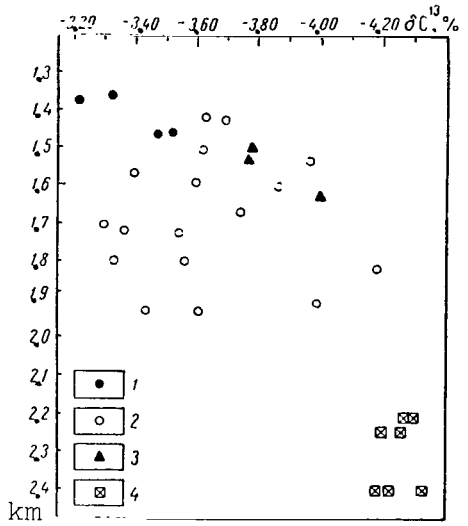


Fig. 71. Comparison of isotopic composition of carbon in ethane with its bedding depth (Permian Ural Area) Petroleum-producing horizons:
1. Middle Carboniferous
2. Yasnopolyanskiy
3. Tournasian
4. Devonian

Devonian gases. On the one hand, they contain the lightest methane (δC^{13}_{av} = -5.22 percent) and ethane (δC^{13}_{av} = -4.26 percent) and on the other hand -- the heaviest of the gases analyzed, propane (δC^{13}_{av} = -2.41 percent) Here were found hydrocarbons (propane) of an isotopic composition (δC^{13} = -1.98 percent), which thus far had not been encountered among sedimentary rock gases.

A comparison of the isotopic composition of gases with their bedding depth does not give satisfactory correlations either based on the entire set of data, or for each productive horizon separately. The observed tendency toward increasing isotopic weight of ethane with depth (Fig. 71) is indirect in nature, since samples from greater depths are represented exclusively by Devonian gases.

The by-product petroleum gases analyzed, being extremely diverse chemically (the nitrogen content ranges from several percent to 90 percent, methane -- from 5 to 50 percent, and

heavy gaseous hydrocarbons -- from 12 to 55 percent) do not disclose a marked relationship between the isotopic composition of carbon with (total) chemical composition.

The crude oils from which the gases analyzed were desorbed have extremely similar isotopic composition of carbon (Table 60), while the isotopic composition of carbon in gaseous hydrocarbons varies significantly. As a rule, crude oils are isotopically heavier than the dissolved gases, however in several cases, especially in the Devonian formations, propane and butane are enriched in C^{13} compared with petroleum overall. The isotopic composition of petroleum carbon does not disclose an intimate relationship with the isotopic composition of the carbon of the gaseous hydrocarbons dissolved therein. However, on the average, Devonian crudes, like Devonian gases, differ in isotopic composition from the crudes from other deposits: they are markedly enriched in the heavy carbon isotope.

Thus, the distribution of carbon isotopes in individual hydrocarbons as a whole is marked by a stable correlation, which is that the low-molecular hydrocarbons are enriched in the light carbon isotopes. However, there is no close correlation between the isotopic composition of carbon in individual constituents and the various parameters characterizing gas composition, and only as a whole for different productive complexes can we note features of the distribution of isotopes in gaseous hydrocarbons.

Carbon Dioxide

Carbon dioxide accompanies methane in natural gas and it is widely distributed in any lithosphere in the diffuse state.

In samples of natural gas studied by R. Zartman et al. [235], [260] the δC^{13} values of carbon dioxide vary from -2.19 to + 1.28 percent. The δC^{13} values we determined for gases of several deposits (Table 61) fall within the same range. On the average, the carbon in CO_2 is 3 percent enriched in the heavy carbon isotope compared with the carbon in methane, while the range of variation of δC^{13} values for carbon in CO_2 is nearly 4 percent. This entirely agrees with the varieties of the CO_2 sources.

In the section dealing with the diagenesis of organic matter (Chapter Three), we showed the possible paths for the influx of CO_2 of different isotopic composition into sediment. Returning to examine Fig. 29, it can be noted that during the formation of secondary minerals and free carbon dioxide the same scheme of carbon isotope fractionation is at work. Formation of the isotopically heaviest carbon dioxide is associated with processes

TABLE 60. ISOTOPIC COMPOSITION OF CARBON IN BY-PRODUCT GASES IN PETROLEUM POOLS OF THE PERMIAN URAL AREA

Deposit	Mean bedding depth, m	Stratigraphic Complex	Gas content in oil, m^3/ton	Gas composition, %					δC^{13}, %					
									Individual hydrocarbons				Gas, total	Petroleum
				CH_4	C_2H_6	C_3H_8	C_4H_{10}	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Aryazhskoye	1390	C_1t	27.4	35.3	12.8	19.3	9.6	18.0	−4.52	−3.78	−3.56	−2.99	−3.53	−2.77
Aspinskoye	1520	C_1jsp	76.0	46.1	16.1	15.0	7.8	10.4	−4.50	−3.93	−3.46	—	−3.60	—
Brusnyanskoye	1610	C_2b	183.6	50.1	18.7	13.9	8.4	4.6	−4.09	−3.09	−2.45	−2.58	−2.74	−2.84
Gremikhinskoye	1405	C_1jsp	11.0	4.8	4.5	5.0	4.3	77.2	−4.86	−3.62	−3.10	−3.20	−3.33	−2.94
Durinskoye	2245	C_1jsp	—	—	—	—	—	—	−4.58	—	—	−2.81	−3.21	—
Kozubayevskoye	1410—1580	C_1jsp	37.0	20.4	12.7	12.2	9.25	36.6	−4.60	−3.66	−3.12	−3.01	−3.42	—
Krasnogorskoye	1265	C_2b	38.7	7.8	13.7	22.7	11.8	37.5	—	−3.32	−2.48	—	—	—
Kuz'minskoye	1730	C_1jsp	34.8	12.3	10.5	19.8	11.7	39.5	−4.84	−4.18	−3.26	−3.12	—	−2.85
Kuliginskoye	1610	C_1jsp	70	45.6	20.3	14.5	7.35	7.1	−4.46	−3.40	−2.78	−2.70	−3.25	−2.77
»	2302	D_3kn	—	36.9	17.5	19.7	7.9	13.9	−4.86	−4.16	−2.18	−2.79	—	−2.79
»	2308	D_3kn	63	36.5	16.5	16.4	8.4	17.1	−5.07	−4.33	−1.98	−2.84	−3.71	−2.79
Kukushtanskoye	1700	C_1jsp	110	54.1	16.6	11.8	6.4	6.8	−4.85	−3.56	−2.81	−2.89	−3.62	—
Lazukovskoye	1370	C_2b	70.0	44.3	14.5	8.35	4.25	25.7	−4.52	−3.50	−2.84	−2.85	−3.24	—
Nozhovskoye	1460	C_1jsp	15.7	8.9	5.95	7.5	2.76	70.5	−4.40	−3.68	−3.31	−2.98	—	—
»	1520	C_1t	9.82	10.0	4.35	3.7	4.25	73.8	−4.34	−4.00	−3.35	−2.89	−3.17	−2.77
Ozhginskoye	1620	C_1jsp	200	54.2	15.5	10.3	6.6	9.8	−4.15	−3.16	−2.61	−2.62	−3.25	−2.68
Ol'khovskoye	1840	C_1jsp	205	50.3	20.4	12.5	6.4	6.8	−5.18	−3.54	−2.81	−2.94	—	−2.89
Severo-Tanypskoye	1430	C_1jsp	35.5	39.7	18.2	16.8	6.7	11.3	−4.52	−3.77	−3.05	−3.13	−3.49	−2.80
Tuivinskoye	2100	D_3p	44.7	42.1	13.2	14.7	7.6	17.7	−5.77	−4.30	−2.39	−3.15	−3.84	−2.84
»	2110	D_3p	—	42.6	13.6	14.9	7.8	16.8	−5.43	−4.28	−2.37	−3.03	—	−2.84
»	2135	D_3p	1	37.9	12.7	15.1	7.6	21.8	−4.98	−4.28	−2.57	−3.03	−3.51	−2.84
Tukachevskoye	1720	C_1jsp	19.7	11.5	7.4	11.7	7.3	57.0	−4.56	—	—	−3.13	—	—
Chernozskoye	1810	C_1jsp	—	—	—	—	—	—	−4.78	−3.98	—	—	−4.44	−3.01
Chutyrskoye	1280	C_2vr	29.0	14.4	16.4	19.6	10.6	33.9	−4.26	−3.22	−2.90	−2.65	—	—
Yumyshskoye	1280	C_2b	—	40.1	21.1	14.0	7.3	13.4	—	−3.52	−2.84	−2.87	−3.84	−2.84
Etyshskoye	1325	C_1jsp	37.1	46.2	13.8	13.25	6.85	16.0	−4.81	−3.66	−3.10	−2.95	−3.27	−2.85

anaerobic decomposition of organic matter and the release of degradative carbon dioxide. Probably, it is precisely this origin that is the basis of the isotopically heavy carbon dioxide (sometimes δC^{13} = + 1.2 percent) in the composition of several natural gases [28, 230]. Possibly, a certain fraction of CO_2 in sedimentary rocks is represented by CO_2 released in the hydrolysis of carbonates according to the scheme $CaCO_3 + H_2O \rightleftarrows CaOH^{\pm} + OH^- + CO_2$, which occurs at temperatures of 100-250° C. This possibility was examined by I. G. Kissin and S. I. Pakhomov. At these temperatures, considering the partition coefficient of carbon isotopes in the system CO_2 - CO_3, carbon dioxide enriched in the heavy carbon /261 isotope relative to the carbonate carbon must be given off. Most of the isotopically light carbon dioxide is formed during the oxidation of organic carbon in the strata. Some of the carbon dioxide can enter sedimentary rocks along with infiltrative water. Its carbon has the same isotopic composition as the carbon of the carbon dioxide from surface groundwater and soil carbon dioxide, that is, on the average δC^{13} = -2.5 percent [25]. Isotopically light CO_2 appears in natural gas via these pathways.

TABLE 61. ISOTOPIC COMPOSITION OF CARBON IN CARBON DIOXIDE PRESENT IN NATURAL GAS

Sampling site	Depth m	Age of deposits	δC^{13}, %		Literature ref
			CH_4	CO_2	
Southern Italy	1552	Miocene	—4.77	—1.29	[129]
» »	2600	Cretaceous	—3.78	—0.87	»
» »	1763	Pliocene	—4.11	—0.91	»
» »	1838	»	—5.24	—0.54	»
» »	1906	»	—4.64	—0.49	»
New Zealand	—	»	—2.50	—0.79	[230]
Hawaiian Islands	—	—	—	—2.44	»
Illinois	40	Quaternary	—7.56	—1.13	»
Texas	3300	Devonian	—4.04	—0.86	»
Zhetybay	2520	Middle Jurassic	—4.09	—0.73	[28]
»	2500	»	—3.87	—2.17	»
»	2260	»	—3.91	—1.86	»
Uzen'	1375	»	—4.35	+0.05	»
»	460	Early Cretaceous	—5.26	—1.67	»
Akkulovka	476	Late Paleogenic	—6.36	—0.56	»
Akzhar	1060	Late Permian	—5.76	—1.46	»

It is essential to note that the broad scatter in δC^{13} values (Isotopically extremely heavy and extremely light samples) characterizes, as a rule, the carbon dioxide contained as a small impurity in natural gas. In those cases when the carbon dioxide

is a predominant constituent, it has a more constant isotopic composition, approximating δC^{13} = -0.7 percent. An example can be the gas pool that consists nearly entirely of CO_2, in Tampico (Mexico) -- one of the largest deposits of this type, with an area of nearly 400 km^2, confined to a thick stratum of Jurassic and Curtaceous limestones. The gas composition (in percent) is: CH_4 - 2.4, C_2H_6 - 0.5, C_3H_8 - 0.9, and CO_2 - 96. The relative content of carbon isotopes in CO_2 determined by W. Lang /189/ corresponds to δC^{13} = -0.68 percent.

Since carbon dioxide is a common link in the turnover of both carbonate as well as organic carbon, the isotopic composition of its carbon on the average reflects the relative contribution of each of these sources. If it is assumed that in accordance with the relative mass of organic and carbonate carbon in sedimentary rocks these contributions appear as 1:4, then we get (assuming for carbonates a mean δC^{13} = + 0.05 percent, and for organic matter δC^{13} = -2.4 percent), the value of δC^{13} = -0.7 percent. It is understandable that approximately the same isotopic composition must be found for the carbon of carbon dioxide released in plutonic thermal metamorphosis of large volumes of sedimentary rocks in which the mean-statistical representativeness of carbonate and organic carbon must lead to the formation of carbon dioxide with δC^{13} = -0.7 percent.

It is curious to note that exactly the same isotopic composition is found for carbon dioxide in two more very important cases: atmospheric carbon dioxide (δC^{13} = -0.7 percent) and endogenic (mantle) carbon dioxide (δC^{13} = -0.7 percent) /267/. As a consequence of this equality, the intensification or weakening of volcanic activity, a reduction or increase in the scales of metamorphosis in particular epochs do not lead to sharp changes in the isotopic composition of carbon in atmospheric carbon dioxide, and therefore, in carbonates and plants. We have written about this /267/. But this deals with the Phanerozoic in which the above-noted ratio of organic and carbonate carbon -- 1:4 -- was established. In the Early Precambrian, poor in organic matter, during metamorphosis the heavier carbon dioxide was given off. /262
This can have led, in the epochs of developed metamorphosis, to heavy carbon enrichment of atmospheric carbon dioxide and, as a consequence, to the deposition of the carbonates particularly enriched in the heavy isotopes. Perhaps, it is here that we must seek the causes of the uncommon enrichment of carbonates in the heavy isotope (δC^{13} = $\pm$ 0.9 percent) which we observed in individual samples of Archaean sedimentary deposits /447/.

Thus, it is obvious that we must take as the "normal" $\delta C^{13}_{CO_2}$ values of gases in sedimentary rocks -0.7 percent. This value

corresponds to the mean isotopic composition of carbon in the stratispheric carbon dioxide. It is precisely this value that the isotopic composition of CO_2 carbon is close to when it forms large accumulations in sedimentary rocks, like the above-noted Tampico pool. But in those cases when CO_2 is present in small amounts, its isotopic composition can depend appreciably on the character of the particular source playing the main role in the given specific instance. Carbon dioxide can be isotopically light if its formation is associated with the processes of the oxidation of organic matter or petroleum, and isotopically heavy, if it is the product of the degradation of organic matter or the hydrolysis of carbonates, or if it is of fermentational origin.

Extremely important is the question of whether there is isotopic exchange in the system CO_2 - CH_4. The CO_2 content in the stratisphere on the average is much higher than the concentration of methane and other hydrocarbons, therefore with the broad development of exchange processes the isotopic composition of methane carbon would be substantially altered, which would render the isotopic analysis of gases unpromising for genetical comparisons.

As follows from Table 61, no relationship of any kind is observed between the isotopic compositions of carbon in CO_2 and in CH_4.

In our view, a convincing proof of the absence of exchange in the inorganic system CO_2 - CH_4 at low (down to 150-200° C) temperatures is the following fact we have found /28/. When the isotopic composition of methane and carbon dioxide present at the same time in isolated gas inclusions in igneous rocks were analyzed, it was found that the difference in the δC^{13} values of the coexisting CH_4 and CO_2 does not exceed 1.9 percent, which corresponds to a partition coefficient of 1.019 and an equilibrium temperature of 325° C. Still, the intrusion from which the samples were taken, even hundreds of millions of years ago, beginning with the Devonian, was in a cooled state and isotope fractionation must have been much greater if there had been the CO_2 - CH_4 exchange at the relatively low temperatures of the cooling intrusion.

Genetical Factors of the Formation of the Isotopic Composition of Carbon in Gases /263

Experimental Study of Carbon Isotope Fractionation in the System CH_4—C_2H_6—C_3H_8—C_4H_{10} At Different Temperatures

An analysis of the isotopic composition of carbon in individual gaseous hydrocarbons shows that in spite of the fairly wide range in variations of δC^{13} values characterizing each constituent, methane, ethane, propane, and butane on the average form a regular series.

Application of thermodynamic isotopic analysis to a natural system requires that we know the rates at which equilibrium is attained, that is, the rates of isotope exchange of carbon at different temperatures, without which we cannot draw a boundary between the thermodynamic and kinetic causes of isotope fractionation in natural hydrocarbons. Accordingly, the experiments described below were set up. In a special autoclave, we observed a variation in the isotopic composition of carbon in methane, ethane, propane, and butane dissolved in petroleum (experiment I) and forming a gaseous mixture in the presence of water vapor (experiment II) at different temperatures. Experiments were conducted at temperatures of 25, 150, 300, and 500° C. In each case the mixture was exposed for four hours.

Petroleum from the Ozhginskoye Deposit (square 13) from the strata of the Bobrikovskiye horizon of the Visean Stage was used for the analysis; the perforation interval was 1618-1622 m, petroleum specific gravity -- 0.8419 g/cm^3, and gas saturation pressure -- 132.5 kg/cm^2. The petroleum was sampled with a stratal sampler and brought to the laboratory in conditions corresponding to its bedding conditions in the stratum (stratal pressure 170 kg/cm^2), and the stratal temperature was 25° C. The sampler was connected into the system shown in Fig. 72. With /264 press 1, the pressure in the system was raised to 200 kg/cm^2. Since the gas saturation pressure in this petroleum was 132.5 kg/cm^2, at a pressure of 200 kg/cm^2 all the gas in the petroleum was in the completely dissolved state. Through valve 7 the petroleum was fed into the heater, where it was kept at a fixed temperature for four hours. Then through valve 9 the petroleum was bypassed into the vacuum trap 12 where it underwent degassing, and the released gas was collected in the gas flow meter 13. During this procedure, and also during the heating the pressure by means of the press was kept at the same level -- 200 kg/cm^2.

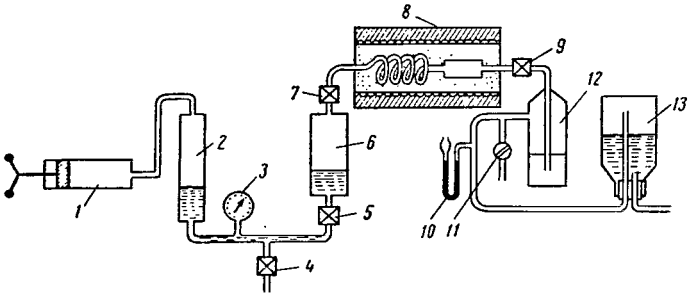


Fig. 72. Scheme of setup for experiment on the carbon isotope fractionation in hydrocarbons CH_4, C_2H_6, C_3H_8, and C_4H_{10} dissolved in petroleum at 200 kg/cm^2.

1. Press
2. Oil-water separator
3. Manometer
4. Valve to water inlet line
5 and 7. Sampler valves
6. Samplers
8. Heater
9. Heater discharge valve
10. U-shaped manometer
11. Valve to vacuum line
12. Trap
13. Gas flow meter

After each experiment, a chromatographic monitoring of gas composition was carried out. The gas phase in the initial hydrocarbon mixture consisted of CH_4 - 54.2 percent, C_2H_6 - 15.5 percent, C_3H_8 - 10.9 percent, C_4H_{10} - 6.6 percent, C_5H_{12} - 3.0 percent, N_2 - 9.8 percent, and H_2S - 0.6 percent. The gas saturation of the petroleum at 25° C was 148 cm^3/g.

After heating at 150° C, the gas factor remained at its former value -- 148 cm^3/g; the gas composition remained unchanged. At 300° C, the gas factor rose to 164.1 cm^3/g, but the constituent composition remained practically unchanged. At 500° C, coke was formed in the heater, there was a sharp rise in the gas yield -- 545 cm^3/g, and hydrogen and unsaturated hydrocarbons appeared in the gas composition.

The other series of experiments (experiment II) were conducted with a gas mixture. Dry gas obtained by contact degassing of the same petroleum from the Ozhkinskaya Deposit was conveyed in a 3-liter contained of stainless steel, where it was heated to 150, 300, and 500° C for four hours in the presence of water vapor (20 g).

At 150 and 300° C, the volume (reduced to normal conditions) and the relative content of the gas constituents studied remained unchanged. At 500° C, the experiment was accompanied by a sharp rise in pressure. The volume of the gas mixture rose to 6150 ml while the initial volume of the hydrocarbon gas was 3000 ml. The gas released after the experiment was opaque and contained products with the characteristic odor or cracking gasoline. Chromatographic analysis showed that present in the products was hydrogen, carbon

dioxide gas, ethylene, and a reduced content of propane and butane. The gas mixture, after the final heating, was separated by means of a chromatographic column into individual constituents: methane, ethane, propane, and butane. Hydrocarbon samples underwent mass-spectrometric isotopic analysis for carbon.

The experimental results are given in Table 62.

The data obtained suggest the following conclusions.

1. At 150° C no change in the isotopic composition of the constituents occurs, compared with the initial constituents.

2. At 300° C, the isotopic composition of the constituents changes slightly. The nature of the variation in experiments I and II is somewhat different. In experiment II with the gas mixture there was a drop in the content of C^{12} in methane and ethane, along with a corresponding rise in its content in propane and butane. In the case of the oil-gas mixture (experiment I), depletion of the C^{12} isotope in methane was observed, while there was an unchanged content or even some depletion of the remaining constituents in C^{12}. /266

3. At 500° C, in both cases all the analyzed constituents are depleted in the light isotope, and in the oil-gas mixture this tendency is much more sharply pronounced.

Thus, the alteration in the isotopic composition of the hydrocarbon constituents analyzed is observed, beginning at 300° C, that is, starting at a temperature corresponding to the beginning of the cracking process. At 500° C there is an enrichment of the gas phase overall in the heavy isotope, that is, the process is not confined to the redistribution of isotopes in the system

$$CH_4 - C_2H_6 - C_3H_8 - C_4H_{10}.$$

During the cracking process, the following reactions can take place:

a) decomposition-recombination

$$CH_4 \rightleftarrows CH_3^{\cdot} + H^{\cdot};$$

$$C_2H_6 \rightleftarrows C_2H_5^{\cdot} + H^{\cdot};\quad C_2H_6 \rightleftarrows CH_3^{\cdot} + CH_3^{\cdot};$$

$$C_3H_8 \rightleftarrows C_3H_7^{\cdot} + H^{\cdot};\quad C_3H_8 \rightleftarrows C_2H_5^{\cdot} + CH_3^{\cdot};$$

$$C_4H_{10} \rightleftarrows C_4H_9^{\cdot} + H^{\cdot};\quad C_4H_{10} \rightleftarrows C_3H_7^{\cdot} + CH_3^{\cdot};\quad C_4H_9^{\cdot} \rightleftarrows C_2H_5^{\cdot} + C_2H_5^{\cdot};$$

b) formation of olefins

$$C_3H_8 \longrightarrow CH_4 + CH_2 = CH_2;$$

$$C_4H_{10} \longrightarrow C_2H_6 + CH_2 = CH_2;$$

TABLE 62. RESULTS OF EXPERIMENTAL STUDY OF CARBON ISOTOPE FRACTIONATION IN THE SYSTEM CH_4—C_2H_6—C_3H_8—C_4H_{10} AT DIFFERENT TEMPERATURES

Experiment I. Hydrocarbons Dissolved in Petroleum, Reactor Pressure 200 kg/cm^2

Hydrocarbons analyzed	Isotopic composition δC^{13}, ‰			
	20 °C	150 °C	300 °C	500 °C
CH_4	—4.15	—4.14	—4.07	—3.68
C_2H_6	—3.23	—3.22	—3.20	—2.95
C_3H_8	—2.66	—2.68	—2.62	—1.99
C_4H_{10}	—2.63	—2.64	—2.64	—2.10

Experiment II. Hydrocarbons Form a Gas Mixture in the Presence of Water Vapor, Initial Pressure 1 kg/cm^2

Hydrocarbons analyzed	Isotopic composition δC^{13}, ‰			
	20 °C	150 °C	300 °C	500 °C
$\sum_{n=1}^{n=4} C_nH_{2n+2}$	—3.24 —3.26	—3.26 —3.22	—3.24 —3.15	—2.78 —2.86
CH_4	—4.15 —	—4.05 —4.14	—4.12 —4.08	—3.63 —3.56
C_2H_6	—3.23 —	—3.20 —3.19	—3.16 —3.12	—3.10 —
C_3H_8	—2.66 —2.61	—2.61 —2.61	—2.74 —2.75	—2.67 —2.69
C_4H_{10}	—2.62 —2.67	—2.64 —2.60	—2.67 —2.71	—2.41 —2.43

Remark. The two figures in each box correspond to the parallel experiments.

c) chain polymerization

$$R^{\cdot} + CH_2{=}CH_2 \rightarrow R{-}CH_2{-}CH_2^{\cdot} \xrightarrow{CH_2=CH_2} R{-}CH_2{-}CH_2{-}CH_2{-}CH_2^{\cdot} \rightarrow$$

and so on until breaking of the chain $-R-(CH_2)_n-R'$.

The isotopic constituent of like radicals cleaved from different hydrocarbons is dissimilar owing to the initial difference in the isotopic composition of these hydrocarbons. Accordingly, reactions of the type (a) provide for the mechanism of associative-dissociative isotopic exchange, which to the first approximation leads to the equalizing of the isotopic composition of the system components, and on attainment of equilibrium in isotopic exchange -- to the separation of isotopes in accordance with the thermodynamic isotope effects at the given temperature. We note that these latter effects are small at high temperatures and are responsible for the difference in the isotopic composition of constituents, measurable in only hundredths of a percent.

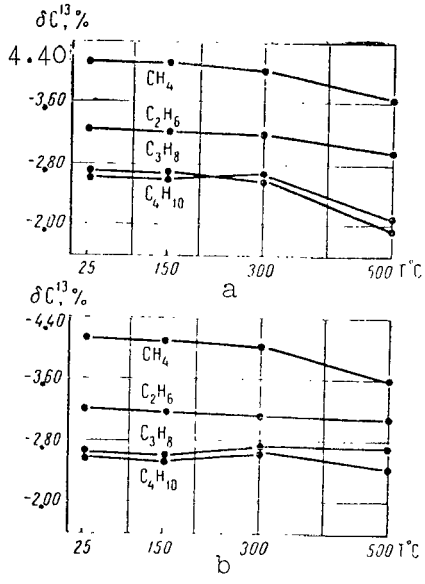


Fig. 73. Variation in isotopic composition of carbon in methane, ethane, propane, and butane with increase in temperature.
a. In the composition of the petroleum-gas mixture at the initial pressure of 200 kg/cm^2 (experiment I)
b. In the gas mixture at the initial pressure of 1 kg/cm^2 (experiment II).

As can be seen from Fig. 73 illustrating the results of the experiment at 300° C, there is a weakly pronounced tendency toward equalizing of the isotopic composition: methane and ethane are somewhat depleted in the light isotope, while propane and butane are enriched in it. The overall isotopic composition of the gas here remains nearly unchanged. Thus, it can be stated that at 300° C there are signs of isotopic exchange. But at 500° C there is the depletion in the light isotope of all system components, without exception. A marked alteration in the isotopic composition of the total gases at 500° C indicates that this system does not remain isolated, that is, the isotope fractionation process is not confined to isotopic exchange. The enrichment $\sum_{n=1}^{4} C_nH_{2n+2}$ in C^{13} involves the departure of some of the carbon from the system CH_4—C_2H_6—C_3H_8—C_4H_{10} in an isotopically light form. /267

Removal of carbon from the system CH_4—C_2H_6—C_3H_8—C_4H_{10}, in all probability, occurs via the stage of olefin formation (b). The

direct isotope effect (both kinetic as well as thermodynamic) of these reactions is slight, that is, the actual formation of the olefins cannot appreciably alter the total isotopic composition of carbon $\sum_{n=1}^{4} C_nH_{2n+2}$. Another observation is central. The origination of olefins in a medium containing free radicals initiates polymerization products, for example, via reaction (c). As a result, the C^{12}-enriched radicals $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, and so on, are removed from the system CH_4—C_2H_6—C_3H_8—C_4H_{10} which leads to C^{12} depletion of the carbon for the system as a whole.

In favor of this mechanism are also results of an analysis of the chemical composition of reaction products in the experiment at 500° C, which revealed the presence of a relatively small amount of olefins (in the form of ethylene in the absence of dienes) and a considerable hydrogen content. This indicates that the olefins formed are continuously expended in polymerization reactions. At the same time the consumption of alkyl radicals in these reactions leads to an excess of hydrogen radicals and shifts the recombination reactions toward the side of hydrogen formation. High-molecular polymerization products have not been identified. /268

It should also be noted that the experiment with gaseous hydrocarbons (experiment II) was carried out in the presence of water vapor. However, the removal of carbon from the system in the form of CO and CO_2, as shown by chromatographic analysis, was slight, even though the presence of water -- in particular, its decomposition, can have made an impression on the general trend of the reactions and on the nature of the synthesized compounds.

Results of the experiment with the gas-petroleum mixture (experiment I), at first glance, appear unexpected. It would appear that cracking of higher hydrocarbons of petroleum must lead to the appearance of a considerable amount of low-molecular fragments. The latter, as usual, are enriched in the light isotope owing to the kinetic isotope effect. A consequence of this would be logically the neo-formation of isotopically light alkanes. However, enrichment of ethane, propane, and butane in the heavy isotope occurred that was even more significant than in the experiment with the gas mixture.

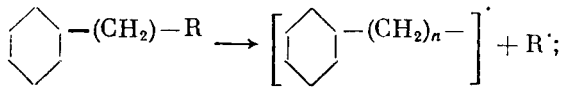
This cracking mechanism suggests the following explanation for this phenomenon. As noted above, during dissociation there is a depletion in the light carbon isotope of all the initial compounds: CH_4, C_2H_6, C_3H_8, and C_4H_{10}. The recombination of radicals provides for the opposite effect. The light isotope depletion of

all components of the system CH_4—C_2H_6—C_3H_8—C_4H_{10} observed in experiment I (500° C) for the petroleum-gas mixture indicate that the compensating role of the radical recombination reactions into lower alkanes in this case is suppressed to a large extent. Obviously, in a complex hydrocarbon system at a pressure above 200 kg/cm^2, the radicals $H^{\cdot}$, $CH_3^{\cdot}$, and so on formed are expended chiefly in reactions of hydrogenation and alkylation of the higher (polycyclic) petroleum hydrocarbons.

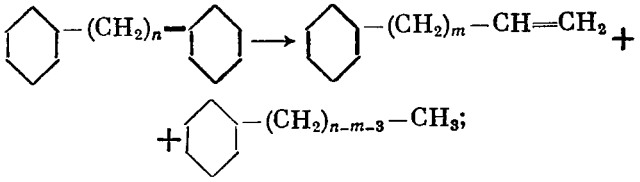
Free radicals in the petroleum-gas mixture are formed not only through the decomposition of the gaseous compounds analyzed, but also through the cleavage of the substituents and the breakdown of the high-molecular petroleum compounds. However, the situation does not extend to the stabilization of these radicals in the form of low-molecular hydrocarbons, since they rapidly enter into addition reactions with high-molecular compounds, thus carrying out processes of disproportionation which lead, on the one hand, to a reduction in the molecular weight of the hydrocarbons, that is, to an increase in the gasoline-kerosene fraction, and on the other hand -- to the formation of condensed structures and coke. Specifically, this is what was observed in experiment I with the gas-petroleum mixture at 500° C, at the conclusion of which a light petroleum product with intense coking of the reactor was obtained. /269

Analogously to the reactions discussed above for the lower alkanes in the gas mixture, in petroleum hydrocarbons the following reactions, for example, can take place:

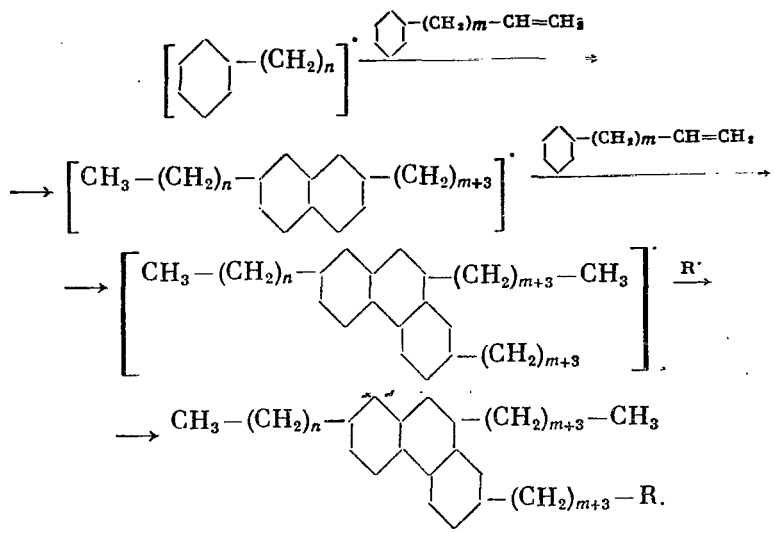
1) decomposition of complex molecules into high-molecular radicals:



2) decomposition of molecules, forming olefins and compounds of lower molecular weight:



3) radical polymerization of olefins, leading -- in particular -- to the formation of condensed structures:



Thus, the composite summary of the reactions consists in the formation, on the one hand, of a compound lower in molecular weight, and on the other hand, a condensed compound. Here the low-molecular radicals R· are not stabilized as low-molecular (gaseous) compounds, but are involved in the admission reactions. It can be stated that petroleum hydrocarbons serve as a kind of trap for low-molecular radicals, which in the absence of petroleum could have formed gaseous hydrocarbons. This agrees with the fact known from hydrocarbon chemistry that during liquid-phase cracking considerably fewer gaseous products are formed than in vapor-phase cracking. /270

The geological significance of this observation is that it allows us to formulate the following conclusion: the transformation of crudes in the strata is not accompanied by a substantial increase in gas release.

The above-considered reactions, generally speaking, cannot be extrapolated directly to natural conditions, since the decomposition of molecules into radicals is possible in the general case only at high temperatures, while the olefin formation reaction requires energy outlays: at a low temperature in view of the high free energy level, this reaction is thermodynamically forbidden. In particular, the free energy of ethylene becomes less than the free energy of C_3H_8 and C_4H_{10}, at temperatures above 450° C. However, within the scope of the chemical model of the petroleum formation process examined in Chapter Four,

providing for energy transfer in the conjugated system organic matter -- solid phase of rocks through free-radical formation, these processes become possible in low temperature conditios.

Rate of Isotopic Exchange

A central result of the experiments described is that at temperatures up to 300° C during the experimental period, that is, during four hours, there is virtually no isotopic exchange in the system CH_4—C_2H_6—C_3H_8—C_4H_{10}. This involves both the gas mixture as well as hydrocarbons dissolved in petroleum.

Even at temperatures above 300° C the change in the isotopic composition cannot be definitely linked to isotopic exchange, since in practice fractionation begins only with the onset of cracking. Thus, from these data it follows that the rate of isotopic exchange in the system we have examined is low.

A direct estimate of the rate constant in this case is difficult in view of the unconsidered character of the reactions leading to the change in isotopic composition. But several general conclusions are possible:

The constant k of the reaction rate is inversely proportional /271 to the time t during which the given compound reached the concentrations c_0/c:

$$k=\frac{1}{t}\ln\frac{c_0}{c}.$$

Chemical reaction rates as a rule rise with increase in temperature approximately two - four times for every 10°.

By taking the temperature coefficient of the reaction rate as 3, that is, $\frac{k_{T+10}}{k_T}=3$, we can determine the time during which at lower temperatures the same isotope separation would be attained as is attained in four hours at the higher temperatures.

Calculation shows that at 50° C a barely detectable change in the isotopic composition of hydrocarbons corresponding to what was observed in our experiment at 300° C is attained in $350\cdot10^6$ years. Therefore, at 50° C, which corresponds to the bedding conditions of most sedimentary-rock crudes, no appreciable change in the isotopic composition of hydrocarbons through isotopic exchange occurs over a prolonged geologic time. At

100° C the separation corresponding to what was observed in the experiment at 300° C is reached in 1.5 million years, and at 150° C -- in 6000 years. In the latter case a marked isotope separation through isotopic exchange is actually attained in geological conditions.

Table 63 gives the isotope partition coefficients between gaseous hydrocarbons, calculated from the values we obtained for the molecular thermodynamic factors (β_Σ-factors) of normal alkanes.

It should be noted that when the mechanism of intermolecular isotopic exchange is incorporated in the system CH_4—C_2H_6—C_3H_8—C_4H_{10}—C_5H_{12} the characteristic features of the differentiation of the isotopic composition of individual hydrocarbons responsible /272 for the features of their origin will gradually be entirely removed by isotopic exchange.

TABLE 63. PARTITION COEFFICIENTS OF CARBON ISOTOPES IN THE EQUILIBRIUM SYSTEM CH_4—C_2H_6—C_3H_8—C_4H_{10}—C_5H_{12} AND THEIR RELATIONSHIP WITH TEMPERATURE (CALCULATED DATA)

α	Temperature, °C				
	27	127	227	327	427
C_2H_6/CH_4	1.0162	1.0089	1.0053	1.0033	1.0021
C_3H_8/C_2H_6	1.0061	1.0033	1.0020	1.0011	1.0008
C_4H_{10}/C_3H_8	1.0030	1.0017	1.0010	1.0008	1.0004
C_5H_{12}/C_5H_{10}	1.0019	1.0010	1.0006	1.0004	1.0003

The probable distribution of isotopes in hydrocarbons constituting this system is caused only by temperature conditions and by the degree of attainment of equilibrium of isotopic exchange. At equilibrium the isotopic shifts must correspond to the coefficients listed in Table 63. Accordingly, we point to one possibility.

We know that the rate of isotopic exchange depends on the rate of the chemical reaction supporting the exchange, where isotopic equilibrium is established always after chemical equilibrium.

For a reaction of the type

$$mAX_n + nBX_m^* = mAX_n^* + nBX_m$$

there exists a relationship linking the rate of isotopic exchange with the rate of the reaction leading to it /8/:

$$-\ln(1-z)=\frac{am+nb}{ab}\omega t,$$

where z is the degree of completion of isotopic exchange, which is defined by the ratio of the proportion of isotopic molecules

$$x=\frac{[AX_n^*]_t}{[AX_n]_t}$$

at a given moment to the proportion of isotopic molecules when isotopic exchange equilibrium is reached

$$x_\infty=\frac{[AX_n^*]_{t=\infty}}{[AX_n]_{t=\infty}},$$

where a is the concentration of the compound AX_n; b is the concentration of the compound BX_n; m and n are the numbers of the exchanging atoms; ω is the rate of the chemical reaction; and t is time.

If the isotopic exchange reaction $C^{13}H_4 + C_2^{12}H_6 \rightleftarrows C^{12}H_4 + C_2^{13}H_6$ is carried out through the radical reaction of the type

$$C_2H_6 + CH_3^{\cdot} = CH_4 + C_2H_5^{\cdot},$$

the rate of this reaction ω is $k\,[C_2H_6]\,[CH_3^{\cdot}]$, where k is the rate constant.

Hence

$$-\ln(1-z)=\frac{[C_2H_6]+2[CH_4]}{[C_2H_6]\,[CH_4]}\,k\,[C_2H_6]\,[CH_3^{\cdot}]\,t.$$

If exchange occurs with a substantial methane excess, then /273

$$z\approx\frac{\alpha\left(\frac{C_2H_6}{CH_4}\right)_t}{\alpha\left(\frac{C_2H_6}{CH_4}\right)_{t=\infty}}$$

and

$$-\ln\left(1-\frac{\alpha_t}{\alpha_\infty}\right)=\left(2+\frac{[C_2H_6]}{[CH_4]}\right)k\,[CH_3^{\cdot}]\,t.$$

If isotope separation reflects the degree of incompleteness of the isotopic exchange process, the resulting equation allows us to determine the actual concentration of radicals. We find the falue α_t through measuring the isotopic compositions of hydrocarbons in a natural sample; α_∞ is the calculated thermodynamic isotope effect for the given temperature (see Table 63); the rate constant of isotopic exchange can be determined experimentally or, from general considerations $k = ae^{-\frac{\epsilon}{RT}}$, where the pre-exponential cofactor a is of the order of 10^{13} $cm^3/sec \cdot mole$; and the energy of activation for radical reactions of the type $C_2H_6 + CH_3^{\cdot}$, ϵ = 14.5 kcal/mole.

The time t denotes the time during which the given atoms were in the exchange state. If it is found from geological considerations, we can obtain an idea of the actual mean concentration of the radicals. This value, in turn, can be used to calculate the rate of different chemical processes (with consideration of free radicals) occurring in natural conditions, and hence -- -- for interpreting the mechanism of hydrocarbon formation.

Obviously, the solution to the reverse problem is also $[CH_3^{\cdot}]$ possible in principal: if by some means we find the concentration of free radicals, for example, through solving the direct problem for a large number of cases, then knowing the mean value of

for different conditions, we can calculate t, that is, we can arrive at the age of the pool.

Of course, these possibilities are to some extent speculative, since their practical realization is complicated by a large number of intervening factors. But it is useful to direct attention to the actual existence of such possibilities.

Intramolecular Biogenic Isotope Effect. Dependence of Isotopic Composition of Gas on Degree of Metamorphosis and the Nature of Organic Material

Previously, usually two possible causes of the chemical fractionation of carbon isotopes in systems of the type CH_4-$-C_2H_6-C_3H_8-C_4H_{10}\ldots$ were considered -- the kinetic isotope effects and the dynamic isotope effects (fractionation caused by isotopic exchange). The conception of the intramolecular distribution of isotopes which we examined and outlined briefly in Chapter Two allows us to bring into consideration a third factor -- isotopic nonuniformity of the original organic compounds. /274

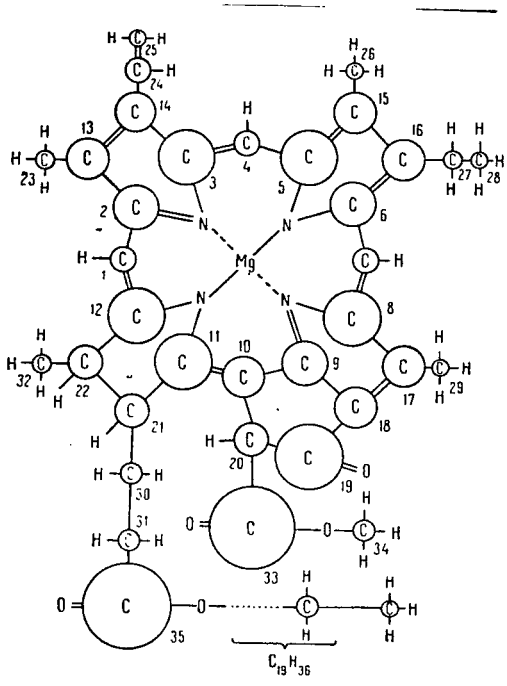


Fig. 74. Example of intramolecular distribution of isotopes in an organic compound (porphyrin)
The diameter of the circles denoting the carbon atoms is proportional to the β_i-factors, that is, it corresponds to the relative C^{13} enrichment of carbon in the given structural position. The number of the atoms corresponds to the number of the β_i-factors in Table 28 which gives the numerical values of the β_i-factors of porphyrin.

The reasons, essentials, and nature of the intramolecular isotopic nonuniformity of organic compounds was discussed in Chapters One-Three. Here we point only to several consequences of this phenomenon that are central to the geochemistry of natural gases.

Fig. 74 shows the intramolecular distribution of carbon isotopes in an organic compound (in this case, in a porphyrin molecule). The size of the circles corresponding to the carbon atoms are given as a function of the β_i-factor characterizing the atom in the given position: the larger the β_i-factor (circle radius), the higher is the relative concentration of the C^{13} isotope in this position. The isotopically lightest carbon is associated, as shown in Fig. 74, with the CH_3 groups that occupy a peripheral position in the molecule. This situation is characteristic not only of porphyrin, which was taken as an example, but also for any other, including highly complex, organic compounds.

The formation of methane during the transformation of organic matter occurred above all through the splitting off of these peripheral CH_3 groups. The thermodynamic isotopic factor characterizing CH_3-group carbon is $\beta_{CH_3} = 1.131$. /275

The thermodynamic isotopic factor of porphyrin overall (excluding the phytol chain) is $\beta_\Sigma = 1.162$ (see Table 28). Above we established that approximately the same β-factor ($\beta_\Sigma = 1.165$) characterizes

humified organic matter (coal in early stage of coalification), on the average. The intramolecular thermodynamic isotope effect in accordance with Eq. (II.28) is $\alpha_{CH_3} = \beta_\Sigma/\beta_{CH_3} = 1{,}031$, and the isotopic shift is $\Delta C^{13} = -3.1$ percent. Therefore, methane formed through the cleavage of the peripheral CH_3 groups proves to be enriched in the light isotope C^{12} relative to the initial organic matter by more than 3 percent, just through the intramolecular isotopic nonuniformity, without considering any kinetic isotope effects.

We recall that we gained the right to speak about the distribution of carbon isotopes in an organic compound in accordance with the calculated values of β_i-factors, on being convinced that biogenic isotopic equilibria exist (see Chapters Two and Three).

The phytol residue, which is essentially a paraffinic hydrocarbon (isoprenoid structure), has a β-factor of 1.150 (see Table 28), that is, the isotopic shift between this hydrocarbon chain and the porphyrin nucleus $\Delta C^{13} = -1.1$ percent. If we assume for the porphyrin ring that simulates our organic matter in general a value of the isotopic composition $\delta C^{13} = -2.0$ percent, for methane we get $\delta C^{13} = -5.1$ percent, while for a high-molecular hydrocarbon of the same kind as petroleum hydrocarbons, $\delta C^{13} = -3.1$ percent. Thus, from the concept of intramolecular isotopic nonuniformity, we arrive at the isotope distribution that actually is characteristic of natural gas, petroleum, and organic matter.

With increasing transformation of organic matter in the strata, the intramolecular isotope distribution primordially intrinsic to it is altered to a large extent. This leads to a change in the isotopic shift in the gases released. Therefore, there must be a relationship between the isotopic composition of the generated gas and the degree of transformation of the initial organic matter.

If, for example, there is the aliphatic chain

$$\begin{array}{l} CH_3-CH_2-\ CH_2\ -\cdots\sum C_nH_{2n+2} \\ \beta_i\,(1{,}131)\ (1{,}149)\ (1{,}151)-\cdots\beta_\Sigma\,(1{,}151), \end{array}$$

then initially the methane formed through cleavage of the extreme CH_3 group will have an isotopic shift ΔC^{13} caused by the intramolecular nonuniformity of -2.0 percent. After removal of this group, the carbon atom of the CH_2 group formerly in the β-position will occupy the extreme position. The intramolecular distribution of isotopes attained during biosynthesis is preserved metastably in subsequent dissociative processes. Therefore carbon of the /276 newly formed peripheral group will be characterized by its former β-factor (1.150).

Through cleavage of this group and the new generation of methane, the isotopic shift in methane will be -0.2 percent, that is, an isotopically much heavier methane will be formed. This is the simplest example. Using the isotopic bond numbers, it is not difficult to arrive at the same conclusion, by combining the mechanisms of dissociation and various initial structures of organic compounds.

Essentially, the general rule is a decrease in the degree of biogenic intramolecular isotopic nonuniformity of organic matter as it undergoes a biogenic evolution. Hence we have the successive decrease in isotopic shifts, attaining in the limiting case a zero value in a completely homogenized carbonaceous matter, and the subsequent enrichment of the gases formed in the light isotope, all the way to the complete coincidence of the isotopic compositions of the gases and that of the initial material.

Thus, we have found the necessity of a relationship between the isotopic composition of a gas and the degree of metamorphosis of the organic matter. From an isotopically light methane at the early stages of transformation, the process moves in the direction of forming isotopically heavy methane at the stages of mature and profound metamorphosis. We see further that this is precisely what happens to the isotopic composition of natural gases.

Actual isotopic shifts caused by intramolecular nonuniformity obviously are smaller than those calculated from isotopic bond numbers. The latter correspond to the equilibrium biogenic isotope effect, where the degree of approach to this quantity is determined by the coefficient of biochemical equilibrium -- a quantity that is smaller than unity.

It is important to note that the values of the isotopic shifts observed in the dissociation products of organic matter and caused by the intramolecular nonuniformity of the initial compound do not depend on the reaction temperature (in contrast to kinetic and secondary thermodynamic isotope effects), since the cause of the shifts is associated not with the reaction mechanism or reaction conditions, but with the nature of the initial material. Accordingly, everywhere here we consider thermodynamic isotopic factors and isotopic bond numbers calculated for $T = 300^{\circ}$ K, that is, for temperature conditions in which the biosynthesis of organic matter on the average takes place.

Still, in the very beginning organic matter the intramolecular distribution depends on conditions of biosynthesis, in particular, on temperature. Actually, the lower the temperature the higher the partition coefficients of isotopes and the higher (as we can see, for example, from Table 32) the intramolecular isotopic nonuniformity.

In Chapters Two and Three we showed that biogenic isotopic equilibria occur both on the intramolecular and intermolecular levels in living matter (see Figs. 19-21), as well as more broadly -- between biochemical fractions of organisms and all constituents of metabolism, including the carbon dioxide that serves as the starting material for photosynthesis, shell carbonate, and so on (see Fig. 22). Since the existence of biogenic isotopic equilibria means the distribution of isotopes in accordance with thermodynamic isotopic factors, it is quite understandable that organisms living in a colder environment must differ also by a higher degree of C^{12} enrichment. Results of isotopic analysis of organismic carbon showed that this is actually so. /277

W. Sackett et al. /227/ found that the isotopic composition of marine plankton depends on the temperature of the water in which it lives. For samples of plankton from the equatorial region of the Atlantic Ocean in which the water temperature is about 25° C, the mean value of δC^{13} was -2.17 percent, while plankton from high-latitude regions of the South Atlantic with a water temperature near zero degrees have an average δC^{13} of -2.79 percent. These investigators explain this result by the fact that in cold water the solubility of CO_2 is higher than in warm, and since it was found /195/ that the isotopic composition of phototrophic organisms depends on the abundance of nutrient carbon dioxide, they concluded that this temperature dependence is an indirect manifestation of the dependence of plankton δC^{13} on CO_2 concentration.

From the positions we have developed, all this can be represented somewhat differently. The dependence of δC^{13} on carbon dioxide concentration probably exists as a consequence of the dependence on the abundance of nutrient carbon dioxide shown by the coefficient of biochemical equilibrium κ. The better the conditions of development of an organism, the lower the κ, and the lower the isotopic shift. Hence the possibility of associating the CO_2 concentration with the isotopic composition of organismic carbon. But this is only one aspect of the problem. The actual effect of photosynthesis, since it is isotopic-exchange in nature, is a direct function of temperature, therefore the lower the temperature (and thus, the higher the thermodynamic partition coefficients of the isotope), the isotopically lighter (under otherwise equal conditions) will be organismic carbon.

In Fig. 75 is shown the variation in the theoretically calculated isotopic shifts as the temperature is varied from 0 to 25° C. In this study we present and rely on β-factors only for 25° C (more exactly, 300° K), but the isotopic bond

numbers and thus the β-factors can be calculated for any temperature by the method outlined in Chapter Two. This calculation was carried out for the organic matter which we simulate with the porphyrin molecule. Whereas for 300° K β_{Σ} = 1.162 (see Table 28) for 273° K we get β_{Σ} = 1.186. Hence we can easily calculate /278 the δC^{13}_{theor}, which as Fig. 75 shows us, decrease with increase in temperature. The theoretical values were compared with the measured isotopic shifts between the carbon in plankton living at these temperatures and the isotopic composition of carbon in marine bicarbonate (δC^{13} = -0.2 percent). There is a symbaticity of the corresponding lines.

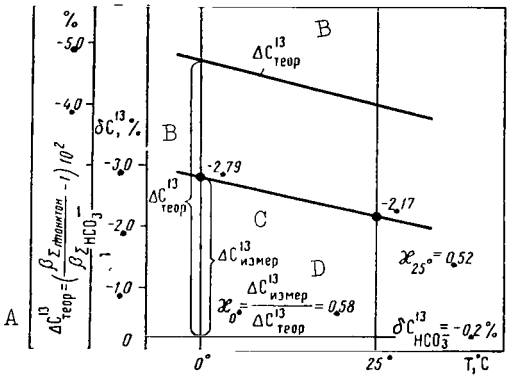


Fig. 75. Comparison of theoretical temperature dependence for thermodynamic isotope effect in the system C_{plank} -- -- HCO_3^- with the experimentally established dependence of the isotopic composition of plankton carbon on environmental temperature

KEY: A. $\Delta C^{13}_{theor} = (\frac{\beta_{\Sigma plankton}}{\beta_{\Sigma HCO_3^-}} - 1)10^2$

B. ΔC^{13}_{theor} C. ΔC^{13}_{meas}

D. $\kappa_{0°} = (\Delta C^{13}_{meas})/(\Delta C^{13}_{theor}) = 0.58$

Thus, the variation in the isotopic composition of organismic carbon with temperature corresponds to a variation with temperature shown by thermodynamic isotopic factors and is caused by the latter. The coefficient of biochemical equilibrium κ also changes somewhat. It is somewhat higher in the case of biosynthesis in a cold environment. Possibly, this is actually associated with the higher CO_2 concentration in cold waters. Dependent on temperature is not only the isotopic composition of organic matter overall (that is, isotope fractionation in the system $C_{plankton}$ - HCO_3^-), but also intramolecular isotopic shifts. And isotopic nonuniformity rises with decrease in temperature. This means that methane formed from organic matter deposited in a cold basin must be, given otherwise equal conditions, isotopically lighter than methane obtained from organic matter deposited in a warm basin. Here let us start from the equality of the isotopic compositions of

either material overall, that is, we are speaking exclusively about an effect associated with the temperature dependence of intramolecular isotopic nonuniformity. This is illustrated by Table 64. But the initial difference in the isotopic composition of organic matter in cold-water and warm-water facies only enhances this effect.

Intramolecular isotopic nonuniformity of organic matter explains to some extent the distribution of carbon isotopes observed in heavy methane homologs. Let us represent the initial organic compound, a compound of aliphatic structure. Each thermodynamic factor can be characterized by $\beta_{\Sigma} = 1.152$. The intramolecular isotopic factor characterizing the carbon in the side or peripheral CH_3 group is $\beta_{CH_3} = 1.131$. The intramolecular isotopic factor characterizing on the average both carbon atoms of the $(CH_3 - CH_2)$-groups, $\beta_{C_2H_5}$, is 1.142. Therefore, if ethane was formed by cleavage of the C_2H_5 group, the calculated isotopic shift must be -1.0 percent. Similarly, if propane was formed through the cleavage of the C_3H_7 group ($\beta_{C_3H_7} = 1.145$), the calculated isotopic shift must be -0.7 percent, while in butane ($\beta_{C_4H_9} = 1.147$) -- -0.5 percent. These data are for 300° K (see Table 64). If we consider organic matter whose biosynthesis occurred at low temperatures (for example, 0° C), we can rely on values of the β-factors calculated for 273° K (see Table 64). In this case the isotopic shifts will be larger. Noting the above-discussed coefficients of biochemical equilibrium for biosynthesis in cold and in warm environments, as well as the mean isotopic compositions of carbon from plankton living in cold and in warm marine basins, we get the distribution of carbon isotopes in hydrocarbons formed from organic matter of both types (see Table 64). /279

A comparison of the calculated isotopic composition from carbon in hydrocarbon gases with the measured δC^{13} of natural hydrocarbons shows that the direction and relative size of isotopic shifts caused by intramolecular isotope effects corresponds to the isotope distribution observed in natural hydrocarbons, namely -- enrichment of gaseous hydrocarbons with the light isotope compared with the initial compound and an increase in the degree of this enrichment in the direction $C_4H_{10} \rightarrow C_3H_8 \rightarrow C_2H_6 \rightarrow CH_4$. /280

Thus, the relationship between the isotopic composition of carbon in gases with the intramolecular isotope distribution predetermines at lease two significant geochemical dependences:

TABLE 64. ISOTOPIC SHIFTS IN HYDROCARBONS CAUSED BY INTRAMOLECULAR BIOGENIC ISOTOPE EFFECTS IN THE INITIAL ORGANIC MATERIAL

Molecule C_nH_m	β-factor of corresponding structural group in org. comp. $-C_nH_{m-1}$		Isotopic shift ΔC^{13}, ‰ $= \left(\frac{\beta_i}{\beta_\Sigma} - 1\right) \cdot 10^3$		Isotopic shift with ref. to coef. of biochem. equilibrium $\varkappa \Delta C^{13}$, ‰		Isotopic comp. of hydrocarbons $\delta C^{13} = \delta C_0^{13} + \Delta C^{13}$		Isotopic composition of hydrocarbon with reference to coef. of biochem equilibrium $\delta C^{13} = \delta C_0^{13} + \varkappa \Delta C^{13}$	
			$\beta_\Sigma = 1.171$	$\beta_\Sigma = 1.152$	$\varkappa = 0.58$	$\varkappa = 0.52$	$\delta C_0^{13} = -2.8\%$	$\delta C_0^{13} = -2.2\%$	$\delta C_0^{13} = -2.5\%$	
	0 °C	27 °C	0 °C	27 °C	0 °C	27 °C	0 °C	27 °C	0 °C	27 °C
CH_4	1.148	1.131	−2.3	−1.9	−1.5	−1.0	−4.2	−3.2	−4.0	−3.5
C_2H_6	1.158	1.142	−1.3	−1.0	−0.8	−0.5	−3.6	−2.7	−3.3	−3.0
C_3H_8	1.162	1.145	−0.9	−0.7	−0.5	−0.4	−3.3	−2.6	−3.0	−2.9
C_4H_{10}	1.165	1.147	−0.6	−0.5	−0.3	−0.3	−3.1	−2.4	−2.8	−2.7

1) dependence of the isotopic composition of gas on the degree of metamorphism of the organic matter: with greater extent of chemical transformation of organic matter, there is a depletion in the light isotope of the gases released; and

2) dependence of the isotopic composition of gas on the origin of the initial organic matter: organic matter formed via the biomass of cold-seas plankton can generate methane and other hydrocarbons that are isotopically lighter than the organic matter deposited in a warm sea. We stress that the latter is due to the difference not in the mean isotopic composition of a given organic compound, but in the intramolecular distribution of isotopes.

Kinetic Isotope Effects in Cracking Processes

Thus far, the kinetic isotope effect has been considered as the main cause of the fractionation of carbon isotopes in the transformation of organic matter. But intramolecular isotopic nonuniformity of the initial organic matter fully explains the correlations that were earlier attributed to the action of the kinetic isotope effect, and does not leave a place for it. Nonetheless, the kinetic isotope effect doubtless does exist and has been often observed experimentally. The cause of this conflict lies, as we see it, in the fact that the sphere of action of the kinetic mechanism of isotope fractionation is much narrower than was assumed.

Below we show that the kinetic isotope effect is virtually absent during the cleavage of low-molecular structures from an organic compound that is polymeric (humic) in character, and is substantially decreased in radical reactions, that is, precisely in the chemical reactions that underlie processes of coalification and petroleum-gas formation. But the kinetic effect "normally" is manifested in dissociative reactions of simple (nonpolymeric) compounds. In this section we look at the results of an experimental study of the kinetic isotope effect in cracking processes.

The role of particular factors in the determination of the final isotope effects depends on the experimental conditions, the kind of compounds, and even -- if we have in mind the intramolecular distribution of isotopes -- on the preceding chemical history of the reagents selected for the experiment. Therefore, data of the experiments described below, strictly speaking, /281 cannot be regarded as the results of studying specifically the kinetic isotope effects, but they do afford an idea about the actual order of magnitude and the kind of isotope effects occurring during the cracking of several typical compounds.

TABLE 65. ISOTOPE EFFECTS (ENRICHMENT OF METHANE IN THE LIGHT CARBON ISOTOPES) DURING CRACKING OF SEVERAL ORGANIC COMPOUNDS

Initial compound	$\Delta C^{13} = \delta C^{13}_{CH_4} - \delta C^{13}_{ini.comp}$, ‰			
	350 °C	400 °C	500 °C	600 °C
n-$C_{18}H_{38}$	−3.38	−2.93	−2.36	−1.81
n-C_7H_{16}	—	—	−0.96	—
n-C_4H_{10}	—	—	−0.97	—
C_3H_8	—	—	−0.38	—
Natural petroleum	—	—	−2.58	—
Shale	—	—	−2.44	—

W. Sackett et al. /215, 216/ investigated the isotopic shift in methane generated by pyrolyzing several normal paraffins (Table 65). Cracking took place at 500° C. Normal octadecane underwent cracking in the 350-600° C temperature range.

The values given in Table 65 refer to the initial instant of the process. They were actually calculated from an equation that links the isotopic composition of the methane formed by this instant to the ratio of the molal concentrations of methane and of the initial compound. By definition, the compound found in this way is the kinetic isotope effect of the reaction. It corresponds to the maximum isotopic shift. During the reaction,

the observed effect begins to diminish, since gradually the isotopic composition of the initial compound changes. But the isotopic shift can also change for another reason: for example, through the appearance in the course of the reactions of various intermediate compounds whose cracking is accompanied by effects that differ from that of the compound shown as the initial reagent. W. Sackett et al. observed a variation in the coefficient in the equation $\delta C^{13}_{(CH_4)} = f$ (CH_4/initial compound) at different temperatures in the cracking of n-$C_{18}H_{38}$, which obviously is precisely associated with the change in the nature of the intermediate products at different process temperatures.

With the example of the cracking of n-octadecane we see the dependence of the isotopic shift on temperature. For this case, the investigators proposed the following empirical equation

$$\log|\Delta C^{13}| = -0{,}108\frac{T\,^\circ C}{100} + 1{,}902,$$

with which the experimental data can be extrapolated into the region of lower temperatures. For example, at 100° C isotope fractionation following from the equation is determined by the value ΔC^{13} = -6.2 percent. /282

Experiments showed that the isotope effect depends on the nature of the initial compound. When low-molecular hydrocarbons undergo cracking, lower C^{12} enrichment of methane is observed. It is suggested that this is due to the dependence of the kinetic isotope effect on the bond rupture energy: the lower the bond rupture energy, the greater the isotopic shift. It should be noted that the disposition does not have any theoretical grounds.

Revealingly, samples of petroleum and bituminous clay pyrolyzed at 500° C yield methane having approximately the same isotopic composition as n-octadecane.

D. Frank [148, 149] undertook a similar study with 2,2-dimethylpropane (neopentane). This compound was selected so as to avoid the effect on the final result of the undetermined intermediate products. Fig. 76 shows the resulting dependence of the isotopic shift in methane formed via cracking on the ratio of the molal concentrations of methane and the initial neopentane. From the graph it is clear that experimental data for different temperatures fit on the same curve, that is, the dependence of the isotope effect on temperature is weak.

Table 66, just as Table 65, presents the calculated values of ΔC^{13}, relating to the initial instant of the reaction.

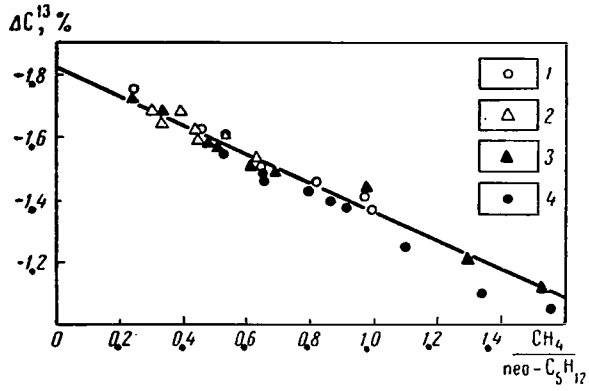


Fig. 76. Isotopic shift $\Delta C^{13}=\delta C^{13}_{CH_4} - \delta C^{13}_{neo\text{-}C_5H_{12}}$ as a function of the ratio of the molal concentrations $CH_4/neo\text{-}C_5H_{12}$ in the cracking of neopentane at different temperatures /149/

1. 500° C 2. 525° C
3. 550° C 4. 600° C

D. Frank /148/ compared his experimental data with the theoretically calculated kinetic isotope effects based on the familiar expression proposed by D. Bigeleisen. /283 As can be seen from Fig. 77, the experimental points are close to the calculated curve, from which D. Frank concludes that the calculated curve can be taken as the temperature dependence of the isotope effect for neopentane cracking. Several values of the isotopic shift in methane calculated on this basis and extrapolated to the low temperature region are shown in Table 67.

A. A. Ivlev /43/, using the approximation in the form adopted by D. Bigeleisen, calculated the kinetic isotope effect for the cleavage not only of methane, but also of other low-molecular hydrocarbons from a hypothetical molecule

TABLE 66. ISOTOPE EFFECT IN THE CRACKING OF NEOPENTANE AND ISOBUTANE

Initial compound	$\Delta C^{13}=\delta C^{13}_{CH_4}-\delta C^{13}_{neo\text{-}C_5H_{12}}$, ‰			
	500 °C	525 °C	550 °C	600 °C
Neopentane	−1,87	−1,81	−1,80	−1,77
Isopentane	−1,37	—	—	—

with infinitely large mass. As follows from Table 68, the isotopic shift decreases in the series $CH_4 \rightarrow C_2H_6 \rightarrow C_3H_8 \rightarrow C_4H_{10}$.

Thus, experimental and theoretical study of kinetic isotope effects in the formation of low-molecular hydrocarbons through cracking shows that the nature and direction of these effects correspond to the distribution of carbon isotopes in natural hydrocarbons.

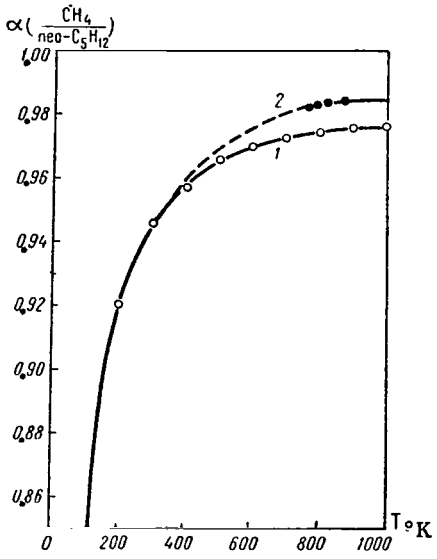


Fig. 77. Comparison of calculated (1) and experimental (2) coefficients of fractionation characterizing neopentane cracking /149/

The most central feature of these isotope effects is their dependence on temperature. The geochemical significance of the temperature dependence is seen in that it enables us to associate the isotopic composition of gases with the temperature conditions of their generation. However, as we noted and will show further, the manifestation of the "normal" kinetic isotope effect is limited in natural conditions. /284

Isotope Effects of Radical Reactions of Hydrocarbon Formation

It would appear that cracking processes of organic compounds satisfactorily simulate natural processes of the decomposition of organic matter, and that the isotope shifts observed in cracking experiments point to the most probable cause of isotope fractionation in natural gases.

However, noteworthy is the fact that both the calculated as well as, which is

TABLE 67. CALCULATED KINETIC ISOTOPE EFFECTS IN THE FORMATION OF METHANE AT DIFFERENT TEMPERATURES

T,K	300	400	500	600	700
ΔC^{13}, %	−5,28	−4,05	−3,38	−2,97	−2,71

TABLE 68. CALCULATED KINETIC ISOTOPE EFFECTS IN THE FORMATION HYDROCARBONS AT T = 300° K

Molecule formed	CH_4	C_2H_6	C_3H_8	C_4H_{10}	$C_{10}H_{22}$
ΔC^{13}, %	−9,5	−6,8	−5,5	−5,0	−4,0

particularly important, the experimentally found values of the kinetic isotope effect considerably exceed the isotope effects observed in natural gases (Table 69). Actually, methane from the upper zone of sedimentary rocks, maximally enriched in the light isotope, is characterized by δC^{13} = -7.0 percent. If we take as the initial material, organic matter with δC^{13} = -2.5 percent, the isotopic shift will be -4.5 percent. The deposits

in which we encounter gas having this isotopic composition have temperatures not above 30-40° C. The isotopic shift calculated based on the above-presented correlation equation will be -8.0 percent for these temperatures, that is, methane with an isotopic composition of the order of -10.5 percent must be formed, which is not observed in nature, at least as a general case. Even for 100° C, which is higher than the temperatures of oil-gas deposits, the isotopic shift ΔC^{13} is -6.2 percent, and the anticipated isotopic composition of methane is δC^{13} = -9.0 percent. /285

TABLE 69. PARTITION COEFFICIENTS OF CARBON ISOTOPES IN LOWER ALKANES, OBTAINED THEORETICALLY, FOUND EXPERIMENTALLY, AND CALCULATED FROM THE RATIOS OF δC^{13}, VALUES OBSERVED IN NATURAL HYDROCARBONS

Method of calculation	CH_4	C_2H_6	C_3H_8	C_4H_{10}
From data on isotopic composition of carbon in petroleum gases. An organic compound with δC^{13} = -2.5 percent was taken as initial compound.	1.021	1.010	1.005	1.003
k_{12}/k_{13} for model of separation from compound of infinitely large mass at T = 25° C	1.095	1.068	1.055	1.050
As above, T = 1000° K	1.033	1.017	1.011	1.008
$k_{12}/k_{13} = K^{0.25}$ at T = 25° C (isotope effect of radical reactions)	1.017	1.012	1.010	1.009
In experiment on cracking of $C_{18}H_{38}$: 25° C	1.080	—	—	—
100° C	1.062	—	—	—
350° C	1.034	—	—	—

Let us assume that no extrapolations of the results of cracking in the low-temperature region are admissible, and the only value δC^{13} = -3.38 percent actually observed in an experiment with n-$C_{18}H_{38}$ at 350° C shows methane generated by a compound with the isotopic composition δC^{13} = -2.6 percent to have δC^{13} = = -6.0 percent. This corresponds to the much higher enrichment in the isotope than is characteristic of most gases in petroleum and oil deposits, even if we neglect the intramolecular isotopic formula.

These facts lead to the thought that simple dissociative reactions of cleavage of low-molecular fragments are not adequate in providing the actual mechanism of the formation of these hydrocarbons in nature.

We attempted to show [32] that a satisfactory explanation can be found if it is assumed that natural hydrocarbons form through radical reactions of the type /286

$$C_nH_m + H^{\cdot} \longrightarrow C_{n-1}H_{2n} + CH_3^{\cdot}. \qquad (a)$$

These reactions differ appreciably from monomolecular reactions of decomposition ($C_nH_{2n+2} \rightarrow C_{n-1}H_{2n-1}^{\cdot} + CH_3^{\cdot}$) in that the free radical here participates as a reactant, which presupposes the production of radicals outside this system.

It is convenient to carry out several manipulations that clarify just what this approach amounts to.

The theory of the transient complex gives the following expression for the rate constant:

$$k = \varkappa \frac{kT}{h} e^{\frac{\Delta S^{\#}}{R}} e^{-\frac{\Delta H^{\#}}{RT}}, \qquad (VI.1)$$

where $\varkappa$ is the coefficient of transmission; k is Boltzmann's constant; h is Planck's constant; R is the gas constant; T is absolute temperature; and ΔS and $\Delta H^{\#}$ are the entropy and heat of activation of the reaction, respectively.

The equilibrium constant of the reaction K is associated with the change in isobaric potential ΔZ by the relation

$$-\Delta Z = RT \ln K$$

or by virtue of the relation $-\Delta Z = -\Delta H + T\,\Delta S$, we can write

$$K = e^{\frac{\Delta S}{R}} e^{-\frac{\Delta H}{RT}}, \qquad (VI.2)$$

where ΔS and ΔH are the change in reaction entropy and enthalpy, respectively.

In the general case, there is no relationship between ΔH and $\Delta H^{\#}$, since the first of these determines the difference in the enthalpy of the products and of the initial reagents (that is, the heat of reaction), and the second determines the difference between the enthalpies of the initial compounds and the activated complex (that is, to the constant term of the activation energy of the process).

However, for a reaction with free radical participation an empirical relationship has been established between the heat of

reaction and the activation barrier. N. N. Semenov [106], based on generalized data for a large number radical reactions, gave the following function: $\varepsilon \simeq 11.5$ kcal $- 0.25\,|q|$, where ϵ is the activation barrier and q is the heat of reaction.

Since the positive heat of reaction corresponds to an enthalpy decrease, for the exothermal reaction we have:

$$\Delta H^{\#} \simeq 11{,}5 - 0{,}25\,(-\Delta H). \tag{VI.3}$$

We introduce this relation into Eq. (VI.1) for the rate constant /287

$$k \simeq \varkappa \frac{kT}{h} e^{\frac{\Delta S^{\neq}}{R}} e^{-\frac{11{,}5-0{,}25\,(-\Delta H)}{RT}}. \tag{VI.4}$$

Referring to (VI.2), we can now represent the rate constant as a function of the reaction equilibrium constant:

$$k \simeq \varkappa \frac{kT}{h} e^{\frac{\Delta S^{\neq}}{R}} e^{-\frac{11{,}5}{RT}} e^{\frac{-0{,}25\,\Delta S}{R}} K^{0{,}25}. \tag{VI.5}$$

The kinetic isotope effect of reaction (a) is determined by the ratio of the probabilities of breaking the bonds C^{12}-C^{12} and C^{12}-C^{13} in the initial compound, that is, by the ratio of the reaction rates of the following isotopic species:

$$\begin{aligned} C^{12}-C_n^{13}H_m + H^{\cdot} &\longrightarrow C^{12}H_3^{\cdot} + C_n^{13}H_{m-2}; \\ C^{13}-C_n^{13}H_m + H^{\cdot} &\longrightarrow C^{13}H_3^{\cdot} + C_n^{13}H_{m-2}. \end{aligned} \tag{VI.6}$$

Referring to Eq. (VI.5) for the rate constant of the reaction activated by the radical, we get:

$$\frac{k_{12}}{k_{13}} = e^{\frac{\Delta S_{12}^{\#}-\Delta S^{\#}}{R}} e^{-\frac{0{,}25\,(\Delta S_{12}-\Delta S_{13})}{R}} K_{12}^{0{,}25} K_{13}^{-0{,}25}. \tag{VI.7}$$

We can neglect the contribution made by the entropy terms in the difference of the reaction kinetics of the isotopic species, therefore

$$\frac{k_{12}}{k_{13}} = K_{12}^{0{,}25} K_{13}^{-0{,}25}. \tag{VI.8}$$

The equilibrium constants for the reactions of the isotopic species expressed in terms of concentration are, respectively:

$$K_{12} = \frac{[C^{12}H_3^{\cdot}]\,[C_n^{13}H_{m-2}]}{[C^{12}-C_n^{13}H_m]\,[H^{\cdot}]}; \quad K_{13} = \frac{[C^{13}H_3^{\cdot}]\,[C_n^{13}H_{m-2}]}{[C^{13}-C_n^{13}H_m]\,[H^{\cdot}]}.$$

The ratio of these constants gives the relation

$$K = \frac{K_{12}}{K_{13}} = \frac{[C^{12}H_3^{\cdot}]\,[C^{13} - C_nH_m]}{[C^{12} - C_n^{12}H_m]\,[C^{13}H_3^{\cdot}]},$$

which serves as the equilibrium constant for the isotopic exchange reaction of the form

$$C^{12} - C_n^{12}H_m + C^{13}H_3^{\cdot} \rightleftarrows C^{13} - C_n^{12}H_m + C^{12}H_3^{\cdot}. \qquad \text{(b)}$$

Hence, we have

$$\frac{k_{12}}{k_{13}} = K^{0.25}. \qquad \text{(VI.9)}$$

Thus, we find that the kinetic isotope effect in type (a) reactions can be expressed in terms of the thermodynamic isotope effect of type (b) reactions. This relationship is formal and is determined by the approximation from which we started, namely by the empirical nature of the relationship between the activation energy and the heat of the radical reactions. /288

Eq. (VI.9) has a somewhat different form for endothermal and exothermal radical reactions. In particular, from the rule of the sign it follows that, given the appropriate selection of reacting and formed radicals, the fragments cleaved can be enriched not only in the light, but also the heavy isotope. Here we will not be diverted by a detailed analysis of this relation and we emphasize the main thing -- the relatively low absolute value of the kinetic isotope effects of radical reactions.

We can express the equilibrium constant of isotopic exchange in reaction (b) in terms of the β-factors of the organic compound and of the radical:

$$K = \frac{\beta_{C_nH_m}}{\beta_{R^{\cdot}}}. \qquad \text{(VI.10)}$$

Either can be found by the method of the isotopic bond numbers. If by C_nH_m we mean a long aliphatic chain, then $\beta_{C_nH_m} = 1.151$. The thermodynamic isotopic factors of the radicals are found as the difference between the thermodynamic isotope factor of the molecule and the isotopic number characterizing the absent bond, for example $\beta_{CH_3^{\cdot}} = \beta_{CH_4} - L_{C-H}$. Using the data for the β-factors of lower alkanes given in Table 15, for 300° K we find $\beta_{CH_3^{\cdot}} = 1.086$, $\beta_{C_2H_5^{\cdot}} = 1.103$, $\beta_{C_3H_7^{\cdot}} = 1.110$, and $\beta_{C_4H_9^{\cdot}} = 1.114$. Substituting these numerical values into Eq. (VI.10) and taking the

quadratic root (raising the expression to the 0.25 power), we get the values of the kinetic isotope effects for the formation of the corresponding hydrocarbons in the radical reactions. The results given in Table 69 show that in this case there is a much better agreement with the partition coefficients observed in natural hydrocarbons for the corresponding compounds.

Thus, the relatively small value of the observed isotopic shifts in methane and other low-molecular hydrocarbons can be explained by a radical mechanism of their formation.

In the preceding chapter we spoke of how the radical reactions are characteristic as a whole for the petroleum formation process. When added together with the foregoing, this means that methane formed by the radical pathway must be genetically linked to other petroleum hydrocarbons. In other words, in the composition of gases, isotopically heavy methane must be accompanied by higher-molecular hydrocarbons. This position, in our view, is well-illustrated by the data of an isotopic analysis of gases associated with bituminous coals. Table 70 gives the results of the isotopic analysis of gases from bituminous coals of western regions of the FRG, very carefully analyzed by U. Colombo, F. Gazzarrini, R. Gonfiantini, H. Knuter, M. Teichmuller, and R. Teichmuller /128/. A well-defined relationship is observed: where ethane and propane are absent in the gas composition or are present in very small amounts, the methane is enriched in the light carbon isotope; but in those cases when the content of ethane, propane, and the higher-molecular hydrocarbons is high, isotopically heavy methane is always present.

Unfortunately, the authors themselves of this remarkable study are prone to explain all their results by the diffusional separation of isotopes, to which in our view they assign an overly high significance. In another study, translated incidentally into Russian and included in the collection Organicheskaya Geokhimiya /Organic Geochemistry/ for 1967, point out that isotope separation of the diffusional type "...is acceptably regarded as the determining factor only of isotope functioning" /91, p. 140/. Somewhat later we examined problems associated with the role of diffusion and kindred mechanisms of isotope separation.

Based on the above theoretical arguments that agree with experimental data, it can be suggested that the inexplicably low (if we refer to kinetic isotope effects) isotopic shifts of methane genetically associated with higher-molecular hydrocarbons are caused by the fact that under certain conditions methane, as is true of other hydrocarbons, forms through radical reactions. /291

A characteristic property of radical reactions of this type, which determines the mechanism of hydrocarbon formation, that is,

TABLE 70. ISOTOPIC AND CHEMICAL COMPOSITION OF GASES DESORBED FROM BITUMINOUS COALS OF THE WESTERN REGIONS OF THE FRG /128/

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Area	Methane in coal ml/g	Hydrocarbon Comp. CH_4	C_2H_6	C_3+	$\frac{C_2H_6}{CH_4} \times 10^3$	$\delta C^{13}CH_4$, ‰
1	2	3	4	5	6	7
Ensdorf, Saar Basin	0.80	80.46	17.25	2.29	214	—2.85
	3.82	81.52	15.80	2.68	194	—3.31
	0.60	49.91	41.70	11.39	889	—2.68
	3.05	78.67	17.50	3.83	222	—3.34
Goettelborn, Saar Basin	1.30	99.34	0.66	—	6.7	—4.78
	0.96	96.68	0.40	0.92	25	—4.49
	0.99	97.53	2.11	1.36	22	—5.62
	0.87	99.10	0.90	—	9.4	—4.69
	1.34	97.96	1.73	0.31	18	—4.12
Luisenthal, Saar Basin	2.92	99.64	0.36	—	3.6	—4.31
	4.95	99.36	0.64	—	6.5	—4.41
	4.28	98.70	1.30	—	13	—4.02
	0.76	95.00	4.58	0.42	48	—3.65
	0.87	89.22	9.48	1.30	106	—3.65
Luisenthal, Saar Basin	2.08	75.06	24.38	0.56	325	—3.48
	4.84	79.11	13.74	7.15	174	—3.61
Kampfhausen, Saar Basin	2.57	56.97	30.50	12.53	535	—2.83
	0.32	30.12	39.99	30.49	1308	—3.48
	0.65	38.32	33.52	98.16	875	—2.52
	1.26	70.03	24.48	5.49	350	—3.01
	3.24	95.12	3.81	1.07	40	—3.82
	1.18	79.25	10.83	9.92	137	—3.73
Friedrich-Henrich, Lower Rhine	1.48	100.00	—	—	0.0	—5.52
	1.47	98.61	1.39	—	14.0	—3.12
	2.55	99.60	0.40	—	4.1	—4.17
	4.86	99.27	0.73	—	7.3	—4.56
	1.08	100.00	—	—	0.0	—6.97
	0.36	100.00	—	—	0.0	—6.31
	1.55	97.43	2.57	—	26	—4.61
Karl Alexandr. Aachen Region	1.46	99.81	0.19	—	1.9	—7.04
	2.19	99.89	0.11	—	1.1	—5.33
	1.57	99.86	0.14	—	1.4	—5.51
	2.20	99.69	0.31	—	3.1	—4.34
	1.61	99.61	0.39	—	3.9	—5.18
Niederrhein, Lower Rhine	0.01	100.00	—	—	0.0	—4.98
	1.43	99.81	0.19	—	1.9	—4.40
	0.01	100.00	—	—	0.0	—5.97
	1.25	100.00	—	—	0.0	—5.50
	0.82	100.00	—	—	0.0	—6.06
	0.82	100.00	—	—	0.0	—5.76
Sofia Jakoba, Aachen Region	1.02	100.00	—	—	0.0	—4.50
	1.94	99.79	0.21	—	2.1	—4.25
Deep well A						
2396 m	10.34	98.66	1.34	—	14.0	—1.68
2954 »	6.39	99.93	0.07	—	0.7	—2.50
3114 »	0.18	94.54	5.46	—	58.0	—2.44
3446 »	1.85	100.00	—	—	0.0	—1.97
3882 »	2.62	100.00	—	—	0.0	—2.38

as we call them, radical-conjugated reactions, is the weakly defined temperature dependence. Radical reactions of this type are pseudothermochemical, that is, their products are present in ratios that are intrinsic to the analogous reactions occurring at high temperatures. Essentially, from this point of view we can also approach the interpretation of the causes for the observed decrease in isotopic shifts in hydrocarbons. If we are diverted from the actual radical mechanism of the decrease in the kinetic isotope effects, by formally assuming a rise in the temperature of the process by some amount ΔT, then at the temperatures corresponding to $T + \Delta T = 1000^{\circ}$ K, the partition coefficients of isotopes are very close to those observed in natural hydrocarbons (see Table 69). At high temperatures, the kinetic isotope effect is not only small in magnitude, but also weakly dependent on temperature. This means that the isotopic composition of methane formed along with other hydrocarbons in pseudothermochemical radical reactions will depend weakly on the temperature conditions in which the hydrocarbons are generated.

Features of Kinetic Isotope Effect of Reactions of Humified Organic Matter

The kinetic isotope effect with respect to carbon is determined by the probability of breaking the bonds $C^{12}-C^{12}$ and $C^{12}-C^{13}$ in a molecule. If a system includes some set of molecules of a given species capable of reacting, then the statistically higher probability that $C^{12}-C^{12}$ bonds will be broken will be expressed in the reaction products being enriched in the light isotope relative to the initial compound. This position is valid for dissociative reactions occurring throughout the volume, such as the cracking of hydrocarbons.

The chemical reaction can also occur via another pathway -- -- for example, at solid surfaces. We know that when crystals are dissolved there is no measurable isotope effect, although the kinetics of the dissolution of the isotopically light species as usual is high. This occurs because dissolution occurs layer by layer. It can be stated that as each molecular layer dissolves, the kinetic isotope effect is present, but since ultimately the /292 entire layer goes into a solution, the resulting isotope effect is absent. This argument, used in a somewhat different sense, is central to understanding the nature of kinetic isotope effects in the processes in which polymerized organic matter of the humus type are transformed and therefore, in the distribution of carbon isotopes in natural gases.

The formation of a given product via the transformation of some individual compound, that is, a compound composed of molecules of the same species, is characterized by a specific fixed energy

of activation. This energy is different somewhat for the isotopically heavy and the isotopically light species, which in fact determines the kinetic isotope effect for the reaction. In complex polymeric compounds of the humus type, elementary structures that can become the starting reagents for the formation of a given reaction product, for example, methane, are in a different position and are conjugated by different types of interaction. Therefore methane forming in this case is characterized not by a single fixed activation energy, but by some more or less broad zone of values. This zone can be subdivided into narrow intervals comparable in magnitude with the isotopic shift in the activation energies. To each such interval there will correspond some set of elementary structures reacting to form methane at a given activation energy, that is, just as in individual compounds and with the kinetic isotope effect intrinsic to this case.

But since these isolated sets of structural species are characterized on the average by different activation energies, they will be brought into reaction at different rates. In other words, the formation of methane from some i-th structural set can be virtually completed by the time when the production of methane from the i + 1-th structural set reaches a detectable value. This situation is analogous to the "layer-by-layer" reaction, which as noted above does not lead to the resultant isotope effect. Therefore in the decomposition products of complex organic polymeric structures, the isotopic shift caused by the kinetic isotope effect must be small.

If the material is an individual compound or mixture of individual compounds, as for example petroleum, the kinetic isotope effect has a "normal" value predicted by the sample dissociative model. The latter, in particular, means that under otherwise equal conditions methane formed through the metamorphosis of crudes must be isotopically lighter than methane produced at mature stages of coalification. The necessity of introducing a restriction concerning the stages of coalification is caused by the fact that at the early stages isotopically extremely light methane is formed not through kinetic isotope effects, but owing to the initially high degree of isotopic nonuniformity of the organic matter. /293

C. Geissler and L. Belau /156/ experimentally analyzed the fractionation of carbon isotopes in artificial coalification. In contrast to the experiments by W. Sackett et al. when individual hydrocarbons and petroleum underwent cracking, in this case a humified substance -- peat moss (Sphagnum polustre) was used as the initial material. The experiments were conducted at 200, 225, 250, and 275° C with different durations -- from 20 minutes to 10 hours. The composition of the gaseous products of coalification was characterized by a large predominance of CO_2 -- approximately 90 percent; the amount of CH_4 was about 2 percent and H_2, 0.5 percent.

One feature of the results in Table 71 that is remarkable, in our view, is that the isotopic shift in methane is extremely slight (ΔC^{13} = 0.1-0.7 percent) at temperatures of 200-275° C. We recall that in the experiments of W. Sackett and D. Frank in the cracking of hydrocarbons, even at 500° C, ΔC^{13} = 1.8-2.5 percent, while the values extrapolated to 200-300° C reached 5-6 percent. It appears to us that this convincingly illustrates the arguments raised above concerning the manifestation of the kinetic isotope effect in humidified organic matter.

TABLE 71. EXPERIMENTS WITH ARTIFICIAL COALIFICATION /1567

Exp. Cond'ns.		δC^{13} of solid coalif. prod.	Gaseous coalification products					
			Yield liters	Chem. comp., %			δC^{13}, %	
T, °C	Duration, min.			CH_4	CO_2	H_2	CH_4 & other HC	CO_2
200	20	−2.74	1.95	1.6	89.9	0.6	−3.45	−2.72
	100	−2.75	2.75				−3.23	−2.75
	600	−2.75	3.6				−3.19	−2.72
225	20	−2.74	2.9	1.8	94.6	0.23	−3.15	−2.70
250	20	−2.73	4.15	1.8	82.6	0.45	−3.00	−2.67
	100	−2.76	4.36				−3.02	−2.61
	600	−2.75	5.0				−2.87	−2.63
275	20	−2.74	4.8	2.0	91.2	0.65	−2.82	−2.59

* HC = hydrocarbons

Remark. The initial substance was peat moss (Sphagnum polustre); elementary composition: C - 50 percent, H - 5.57 percent, N - 0.76 percent, and O - 43.6 percent; constituent composition: hemicellulose - 22 percent, cellulose - 16 percent, lignin - 2.2-4.8 percent, carbohydrates - 4.6 percent, benzene bitumenoid - 2.8 percent, alcohol-benzene bitumenoid - 5.3 percent, humic acid - 12 percent, fulvic acid - 11.8 percent, humins - 6.5 percent, humatomealanic acid - 5.1 percent, humus acids - 6.9 percent, water - 15.94 percent, and ash - 2.92 percent; isotopic composition of carbon overall, δC^{13} = -2.73 percent.

Genetical Scheme of Formation of Gases /294

The isotopic composition of gases in different geologic environments is due to the predominating action in these conditions of a specific mechanism of partition. In particular, the regular variation noted in the isotopic composition of methane with depth is associated with the change across the profile of sedimentary rock in the kind of processes controlling the isotopic composition of methane. Fig. 78 shows the predominant processes of carbon isotope fractionation as a function of the stage of transformation of the organic matter and the type of the initial matter.

In the upper zone of sedimentary rocks is found methane maximally enriched in the light carbon isotope. Besides the intramolecular isotope effect, in these conditions an important role can be played by the intermolecular biogenic isotope effect, associated with the activity of microorganisms. In this case the isotope effect can be greater. It must be remembered that during the chemical (abiogenic) decomposition of organic compound, the isotopic composition of the decomposition products is controlled by the β_i-factor of the initial structural group, and not that of the actual compound formed. For example, since the methane molecule containing a valency-saturated carbon atom cannot be part of a more complex compound, the isotopic composition of methane generated by organic matter is determined not by the β-factor of the methane itself, but by the β_i-factor of the structural groups which is the starting point for methane formation. If methane resulted from a biochemical, fermentative process, its isotopic composition would be determined directly by the intermolecular biogenic isotope effect, and the value of the isotope displacement would be determined by the β_Σ-factor characterizing the methane molecule as such. The thermodynamic isotopic factor /295 of methane -- $\beta_{\Sigma_{CH_4}} = 1.113$ -- is much smaller than the β_i-factor of the CH_3 group (1.131), and when it is cleaved, as shown above, there is a maximum isotopic shift caused by the intramolecular isotope nonuniformity. By comparing $\beta_{\Sigma_{CH_4}}$ and $\beta_{i_{CH_3}}$, it is clear that whereas through the intramolecular isotope effect methane with $\delta C^{13} \approx -5.5$ percent can be formed, fermentative methane must by characterized by δC^{13} values ≈ -7.5 percent.

Thus, the singular enrichment of methane C^{12} in the upper zone of sedimentary rocks can be viewed as resulting from intermolecular biogenic fractionation carried out by methane-producing bacteria (see Fig. 78, Section A).

Earlier we noted /297/ that enrichment in C^{12} of microbiological methane possibly resulted from the equilibrium of isotopic exchange in the system CO_2 - CH_4. The concepts from which we reason here admit of a broader interpretation of isotopic equilibrium as a specific biogenic isotope effect not associated with any specific system, for example, CO_2 - CH_4.

Usually it is held that active microbiological processes die out at depths to 50 m. However, isotopic data show that the thickness of the biochemical zone of methane generation can be considerably greater -- as much as 300-400 m. In the more deeply buried deposits, the mechanism of interbiogenic separation of isotopes is inactivated owing to the dying out of microbiological

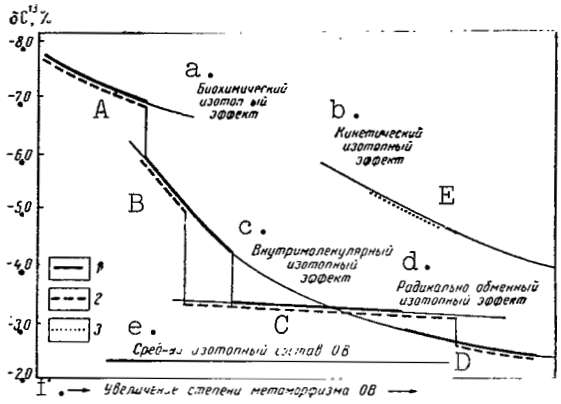

Fig. 78. Dependence of predominant processes of isotope fractionation and the corresponding isotopic shifts in methane carbon on the stage of transformation of organic matter and its nature

1. Humus organic matter
2. Sapropelic organic matter
3. Petroleum hydrocarbons

KEY: a. Biochemical isotope effect
b. Kinetic isotope effect
c. Intramolecular isotope effect
d. Radical-exchange isotope effect
e. Mean isotopic composition of organic matter
f. Increase in degree of metamorphism of organic matter

activity. Further formation of methane is associated predominantly with dissociative processes occurring in humified organic matter. At this stage determining is the isotope fractionation caused by the intramolecular biogenic isotope effect, that is, intramolecular isotopic nonuniformity of the organic matter (see Fig. 78, section B). We will recall that since the initial organic matter has a complicated structure of the humus type, kinetic isotope effects as ordinarily understood (that is, associated with the higher probability of the rupture of the C^{12}-C^{12} bond than of the C^{12}-C^{13} bond) here are absent or reduced to a minimum.

Fig. 74 graphically presents the distribution of the β_i-factors characterizing carbon atoms that occupy different structural positions in a molecule. As we can see, the isotopically lightest carbon is concentrated in the CH_3 groups of the molecules, where this differentiates all compounds. The isotopically heaviest carbon is in the CH_2 groups. The values of the β-factor increase with substitution of the C-H bond by the C-H bond.

The formation of methane from a more complicated organic compound occurs through the cleavage of the carbon-hydrogen groups (CH_3-, CH_2-, and so on). Here the methane inherits the isotopic composition determined by the β-factor corresponding to the structural group. /296

Initially (at the early stages of metamorphism) the beginning organic matter contained a considerable number of CH_3 groups, which cleaved off first, therefore the isotopic composition of methane released at this stage of the transformation of organic matter corresponds to δC^{13} = 5.0 percent (at 25° C). As the organic

matter loses hydrogen and the reserve of CH_3 groups is exhausted, formation of methane increasingly becomes the result of the cleavage of CH_2 groups. The methane released at this stage proves to be isotopically heavier.

The carbonaceous matter in the later stages of metamorphism contains the preserved hydrogen, as a rule, now as part of CH groups, for whose carbon high β-factors are characteristic. Methane genetically associated with the carbon in the structural groups is even more enriched in the heavy isotope.

Thus, the isotopic composition of methane depends on the stage of coalification of the organic matter. It should be stressed that this must be understood as a consequence not of general enrichment of the initial material in the heavy isotope resulting from the preceding role of the isotopically light methane (the calculation shows that this circumstance plays a very slight role, see Chapter Three), but the results of the elimination first of all of peripheral CH_3 groups enriched in the light isotope by way of intramolecular thermodynamic isotope effects. It is here, obviously, that we have the cause of the dependence of the isotopic of gases on their bedding depth that we established earlier and have noted at the beginning of this chapter, since in the general case the degree of transformation of organic matter increases with increasing depth of sediments and increase in temperature.

The dependence of the isotopic composition of methane on the degree of coalification of the organic matter can be established also for more specific examples. An appropriate material for analyzing this dependence is the gas adsorbed in coal whose degree of coalification can be easily estimated and compared with the isotopic composition of gas.

We can take as the coalification parameter the content of volatile constituents: the higher the volatiles, the lower the degree of coalification. Fig. 79 shows the dependence of the isotopic composition of methane on the volatiles content for coals from several western regions of the FRG. By making a comparison for all types of coals overall, U. Colombo et al. noted the unsatisfactory nature of the relationship between the isotopic composition of gases and the volatiles content, explaining this by the "...interference of physical processes such as diffusion and effusion of coal gases during migration" /128, p. 19/. The graph shown in Fig. 79 differs from the original only in that within the general field of points functions are singled out separately for bituminous coals of the Saar Basin and bituminous /297
coals of the Lower Rhine and other regions in the western part of the FRG. In light of the concepts developed in this study,

the mechanism of the formation of the isotopic composition of methane in humolite and bituminous coals in which the gas is enriched in the higher-molecular hydrocarbons must be fundamentally different.

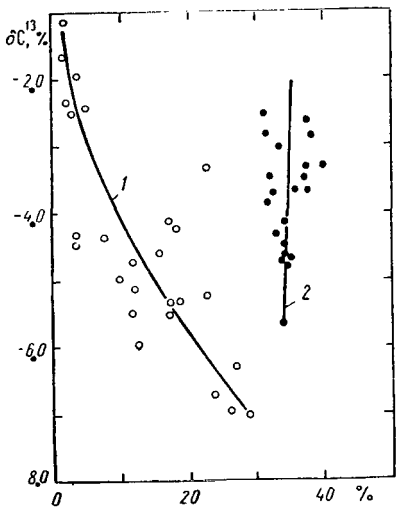

Fig. 79. Comparison of isotopic composition of methane sorbed in bituminous coals with the coalification rank of coal (by the volatiles content in percent)
1. Gases nearly entirely methane (Lower Rhine and other regions)
2. Gases with high content of $C_2 - C_4$ hydrocarbons (Saar Basin)

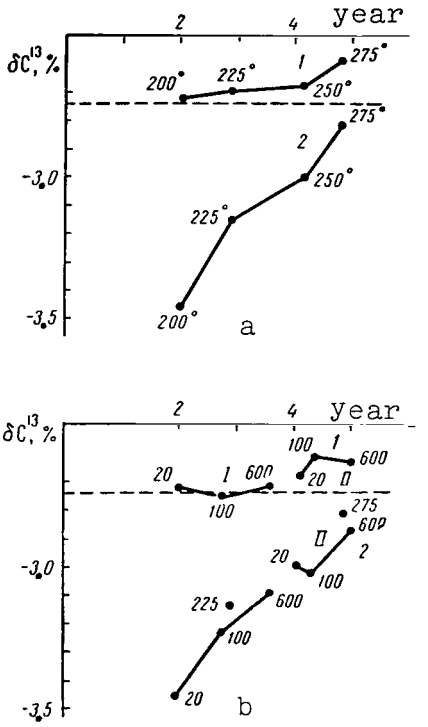

Fig. 80. Results of experiments with artificial coalification /156/
a. Duration of experiment is constant (20 minutes), temperatures differed
b. Temperature constant (I. 200° C, II. 250° C), temperature duration (in minutes) differed
1. CO_2 2. CH_4

As Fig. 79 shows, in those cases when the gas is substantially methane (curve 1), a fairly well-defined dependence of the isotopic composition of methane on its volatiles content is observed, that is, on the degree of coalification. Therefore, by the tendency predicted from an examination of the intramolecular

distribution of isotopes, the methane is enriched in the heavy isotope with increasing extent of transformation of the initial organic matter. Here it is of interest once again to return to a discussion of the results of the experiment by G. Geissler and L. Belau, who analyzed the isotopic composition of gases released /298 during the artificial coalification of a peat bog (see Table 71). Fig. 80 presents the isotopic composition of methane as a function of the total amount of released gas, in this case simulating the degree of coalification. Methane as we can see is enriched in C^{13} with increasing extent of the process.

The experiment's authors explained this as follows. While in the initial stage owing to the predominant rupture of the C^{12}-C^{12} bonds compared with C^{12}-C^{13} bonds, isotopically lighter methane was removed, with time owing to the accumulation in the initial material of C^{12}-C^{13} bonds, the latter were involved in increasingly greater proportion in dissociation; this led to a relative enrichment of the methane released at this stage in the heavy isotope. Moreover, in the view of these investigators, the decrease of the kinetic isotope effect with increase in temperature plays a role. This explanation is based on the concepts of the determining role of kinetic isotope effects, which as we have attempted to show above, are inapplicable in full measure to polymeric organic structures of the humus type.

But if in this case kinetic isotope effects actually had been at work, then this above all would have led to the formation of very light methane (of the order of δC^{13} = -6.0-7.0 percent), as follows from the theory of the kinetic effect and experiments on the decomposition of individual compounds. Moreover, the kinetic isotope effect at temperatures used in the experiment has a strong temperature dependence. From the experiments it is further quite clear that the isotope shifts as a function of temperature are virtually absent, since the points in the graph in Fig. 79 characterizing the different temperature conditions in the experiment relate to the same curves. This means that the isotopic composition of the methane obtained at 275° C will be equal to the isotopic composition of methane formed at 200° C if the duration of the experiment in the latter case is made sufficient to obtain the same amount of gas as at 275° C, in 20 minutes. Therefore, here the temperature plays a role of a factor determining the rate of the process. and not the size of the isotope effect.

It can be noted that in these experiments, even at the initial stage of the coalification, methane was obtained quite heavy ($\delta C^{13} \approx$ -3.5 percent instead of the value of -5.0 percent

and expected from considerations of intramolecular isotope distribution). But this is understandable, since the experiment from its very outset was conducted at relatively high temperatures (200° C), providing the activation energy sufficient to break not only isolated C-C bonds, but also simultaneously two C-C bonds. Because of this, during dissociation from the very outset not only were the isotopically lightest CH_3 groups involved, but also the heavier CH_2 groups. In nature, early diagenesis occurs in low temperature conditions, therefore bond rupture proves to be energetically more successive, and the range of variation in the isotopic composition of methane throughout the coalification is much larger. /299

Thus, at the next stage of the transformation of organic matter following the biochemical stage, which corresponds to the early stage of coalification, the isotopic composition of gases is determined by the intramolecular biogenic isotope effect. With growing coalification, the isotopic nonuniformity of the initial organic matter is smoothed over, the isotope shifts decrease, and ultimately the gas is enriched in the light isotope.

We have been examining the process mostly as concerns methane, but if we turn to oxygen-containing structures and take note of the corresponding isotopic bond numbers, we can easily see that the tendency toward enrichment in the light carbon isotope with increasing coalification is characteristic also of CO_2 (understandably, here the isotopic composition of CO_2 asymptotically approaches a level other than the isotopic composition of CH_4, which was noted in the experiment of G. Geissler and L. Belau).

At a certain stage in the transformation of organic matter the principal phase of petroleum formation commences, according to N. B. Vassoyevich. The corresponding stage of coalification corresponds to coals of grades D, G, and Zh /64/. As we have attempted to show in the last chapter, at this stage the organic matter is chemically prepared to involve the radical mechanism of the liberation of hydrocarbon structures. Here owing to the abrupt decrease in isotopic shifts in the radical process, the methane generated along with other hydrocarbons is enriched in the heavy isotope. Section C in Fig. 78 corresponds to this situation.

The transition to this stage is reached earlier or later, depending on the composition of the initial organic matter. Organic matter that contains abundant hydrocarbon structures, for example, sapropelic type matter, will be involved in the radical-petroleum-producing process sooner (from the standpoint of the degree of metamorphism attained) than organic matter that was initially poor in lipoid constituents.

In Fig. 78, section C corresponding to this case is represented as a line that is nearly parallel to the x-axis, which characterizes the weak dependence of the isotopic shift in gas on the degree of transformation of the organic matter or on temperature conditions. Actually, as was shown above, when methane is generated by the radical pathway, in view of the pseudothermal character of this process its constants, in particular the ratio of the rate constants of the reactions of the isotopic species determining the isotopic shift depend very slightly on temperature. Therefore the isotopic composition of methane formed /300 in this way should not show a substantial temperature dependence.

The process is the same, regardless of whether it occurs with the participation of the diffuse or homogeneous form of organic matter. Methane formed along with petroleum, accompanying petroleum during migration, and present together with it in pools is depleted in the light isotope to the same extent and for the same factors as methane sorbed in bituminous coals if the gas composition of the latter contains high-molecular hydrocarbons, that is, if these coals have reached the stage at which the radical mechanism of the release of hydrocarbon structures is activated.

Turning to Fig. 79, we can note that the abundance of carbon isotopes in gases corresponding to bituminous coals in the Saar Basin (curve 2) is in agreement with the foregoing. The gases sorbed in these coals are marked by increased concentration of ethane and higher hydrocarbons (see Table 70). The methane in these gases is considerably enriched in the heavy carbon isotope. Due to the bituminosity of Saar Basin coals and, therefore, the earlier involvement of the radical mechanism, isotopically heavy methane begins to be generated at a stage corresponding to the lower degree of metamorphism. Finally, there is no dependence of the isotopic composition of methane on the degree of coalification.

Thus, after completion of the biochemical stage, dissociative reactions leading to the liberation of gases are culminated, at least, in two fundamentally different ways.

The first pathway is the formation of methane through a dissociative reaction of the type

$$C_xH_yO_z \longrightarrow C_{x-i-j} + H_{y-4i}O_{z-2j} + iCH_4 + jCO_2.$$

In this case methane is formed as a rule along with carbon dioxide, but cleavage of the methyl radical stabilized in the form of the methane molecule from side chains or end groups of organic compounds can also occur:

$$C_xH_yO_z \longrightarrow C_{x-i}H_{y-4}O_z + iCH_4.$$

The second pathway involves radical reactions requiring a preliminary stage of radical generation. The free valency at the surface of the solid phase can be transferred into the bulk by means of a radical that enters into reaction with the organic matter:

$$C_xH_yO_z + H^{\cdot} \longrightarrow C_{x-1}H_{y-2}O_z + CH_3^{\cdot}.$$

The last reaction can proceed not only with the formation of the radical $CH_3^{\cdot}$ and its recombination with H· in a CH_4 molecule. Other reactions can also occur simultaneously: /301

$$C_xH_yO_z + H^{\cdot} \longrightarrow C_{x-2}H_{y-4}O_z + C_2H_5^{\cdot}$$

or chain development:

$$C_xH_yO_z + CH_3^{\cdot} \longrightarrow C_{x-2}H_{y-4}O_z + C_3H_7^{\cdot}.$$

In other words, in reactions of this type methane is formed together with other heavy homologs.

The paramount difference in these two methods of generating methane, isotopically, is that the methane formed by the first pathway, at the early and middle stages of the transformation of organic matter, is much more enriched in C^{12} than the methane formed by the second pathway.

In nature, these processes can be concomitant. In each case the isotopic composition of methane is the total of the competition of these two types of gas generation. Obviously, methane gases nearly devoid of the heavier hydrocarbons are formed principally by the first pathway. These are the isotopically lightest gases. Oily gases contain methane of dual origin. Evidently, the richer the gases are in the heavy hydrocarbons, the more methane of the second type they contain, and thus, the isotopically heavier will be the carbon of the methane in these gases.

From analyses of the isotopic composition of by-product gases of deposits in Permskaya Oblast, a plot has been made of the isotopic composition of methane as a function of the content of the heavier homologs (Fig. 81). As this graph shows, there is a definite correlation between the isotopic composition of methane and the ratio $\sum_{n=2}^{n=4} C_nH_{2n+2}/CH_4$: the less heavy homologs, the isotopically lighter the methane. However, generally speaking, by-products of crudes are not the most appropriate material to illustrate the above principle.

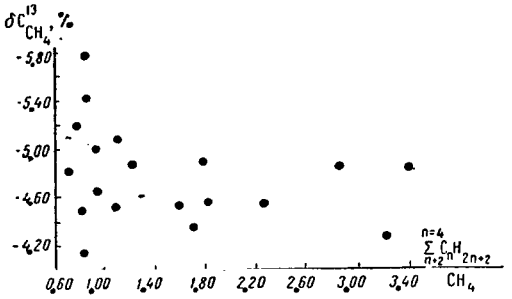

Fig. 81. Relationship of isotopic composition of methane with the hydrocarbon composition of the by-product of oil pools in the Permian Ural Area

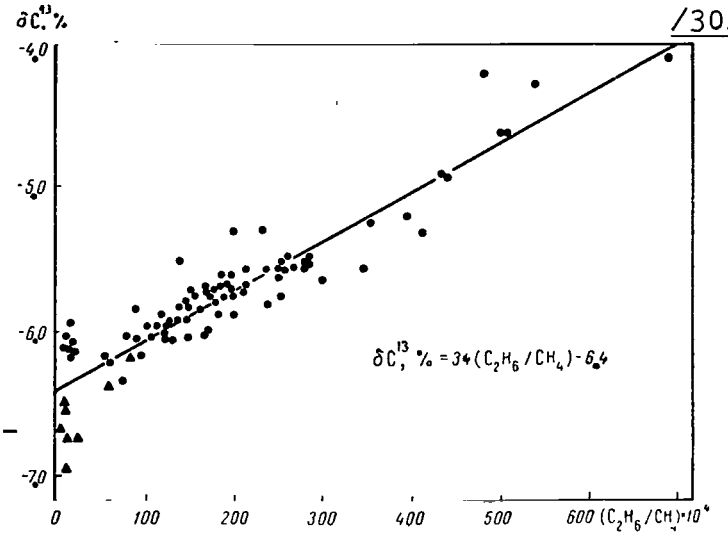

Fig. 82. Relationship of isotopic composition of methane with hydrocarbon composition of gas (gas pools in Southern Italy) /135/

/302

This correlation shows up more distinctly in the example of syngenetic gases, for example, those desorbed from coals. Fig. 82 gives the curve $\delta C^{13}_{CH_4} = f(C_2H_6/CH_4)$, obtained by U. Colombo et al. upon analyzing bituminous coal gases. As we can see, the dependence between the content of the heavy isotope in methane, on the one hand, and the quantitative ratio C_2H_6/CH_4 on the other, is quite strongly expressed. It should be noted that the investigators themselves associate this correlation with the diffusion process.

When there is a very high degree of metamorphism of bituminous coals, gases of chiefly methane composition are again formed. Through the carbonization of organic matter and urtrates of the hydrogen reserve essential to them, the radical mechanism of the release of hydrocarbon structures is disengaged, corresponding to culmination of the principal stage of petroleum formation according to N. B. Vassoyevich. Section D in Fig. 78 corresponds to this stage. It serves as a continuation of curve B. To put it another way, here isotopic shifts, as in the early stages of coalification, are determined by the intramolecular isotope effect. However, by the time the stage of coalification close to the anthracite stage is reached, the intramolecular isotopic nonuniformity becomes so minor that the isotopic shifts caused by /303 it lead to virtually no enrichment of the gas in the light carbon isotope. As a result, isotopically very heavy methane is formed, virtually coinciding in the isotopic composition of carbon with

the initial coal. An example of this kind can be taken as the gas accumulations in the northern part of the FRG which owe their origin "...to processes of coalification of strongly carbonized organic matter" /139/.

TABLE 72. ISOTOPIC COMPOSITION OF METHANE GAS (IN PERCENT) FROM DIFFERENT HORIZONS OF DEPOSITS LOCATED BETWEEN WESER AND EMS /222/

Borehole number	Perforation interval, m	Strata			
		Zollin-gen	Hardeg-sen	Detfurt	Wolpri-hausen
7a	2186—2198	—2,66	—	—	—
1	2198—2285	—2,61	—	—	—
7в	2294—2305	—	—	—2,58	—
5	2511—2519	—	—	—2,58	—
6	2590—2602	—2,52	—	—	—
3	2603—2610	—	—	—2,55	—
4	2598—2647	—	—2,49	—	—
2	2627—2641	—	—	—	—2,58
9	2652—2669	—2,50	—	—	—
8	2667—2673	—2,49	—	—	—

Table 72 gives the results obtained by W. Stahl of an isotopic analysis of gas from the gas field located in the confluence of the Weser and Ems rivers (FRG).

These gases are characterized by an unusual enrichment of methane carbon in the heavy isotope. But the formation of gases having this isotopic composition must necessarily derive from the essentials of the scheme examined here.

Methane of the later stage of metamorphism of organic matter is isotopically heavier than the methane of the hydrocarbon stage (see Fig. 78). Whereas at the early stage methane obtained through dissociative reactions is isotopically lighter than the methane obtained via radical reactions, at the late stage the relationship is reversed. This means that whereas the isotopic composition of gas from the late and middle stages of metamorphism was formed through the competition of processes of both types, methane present in dry gas freed of the higher-molecular hydrocarbons will be isotopically heavier than methane in oily gas. Therefore, we must obtain a picture that is the opposite of the one that we arrived at by employing similar arguments with respect to the early stage of coalification. Actually, W. Stahl in a paper on the origin of gas deposits in the northwest part of the FRG /222/ obtained a dependence (Fig. 83) of the isotopic composi- /304

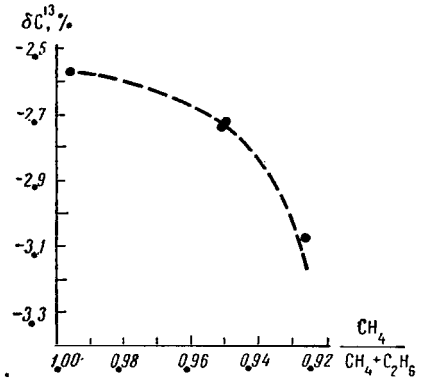

Fig. 83. Relationship of isotopic composition of CH_4 with hydrocarbon composition of gas (Northwest German Basin) /222/

tion of methane on the ratio C_2H_6/CH_4 which is inversional in character compared with the dependence of the kind established by U. Colombo et al. for natural gases in Southern Italy or for gases desorbed from coals of lower grades.

Thus, we find that gases from the early and middle stages of the transformation of organic matter are characterized by a direct dependence of the type $\delta C^{13}_{CH_4} = f\left(\frac{C_2H_6}{CH_4}\right)$ (see Fig. 82); for gases from the middle stage of metamorphism a function of this type is uncharacteristic (see Fig. 81); gases from the late stage of metamorphosis are characterized by the reverse function, of the type $\delta C^{13}_{CH_4} = f\left(\frac{C_2H_6}{CH_4}\right)$ (see Fig. 83). The manifestation of a function of this type in by-products of petroleum must be attributed to the presence therein of a gas impurity formed in the nonhydrocarbon phase. In particular, the weak direct correlation disclosed in by-gases from deposits in Permskaya Oblast (see Fig. 82) can serve as an indication that there is an impurity of gases from the early stage of coalification.

Besides the processes of gas formation associated with diffuse organic matter and coal, whose mechanism -- at least from the standpoint of the formation of the isotopic composition of gases -- appears identical, we must look at the possibility of gas forming through the degradation of crudes. Some investigators place very great significance on this method of gas formation. A. F. Dobryanskiy, in elaborating the concept of the methanization of petroleum as a final stage in its transformation, suggested that "...natural gas and liquid petroleum must be considered as a single complex, and that -- with the exception of purely biogenic methane -- natural gas has a petroleum origin" /55, p. 71/. V. A. Sokolov criticized this point of view /305
"...essentially denying the possibility that methane formed directly from the organic matter in rocks" /110, p. 201/, reasoning above all from quantitative ratios of the content in sedimentary rocks of methane and petroleum hydrocarbons.

But isotopic data more definitely indicate that natural gas, including by-product petroleum gas and gas from gas caps of oil-gas deposits for the most part was formed not from petroleum /287.

In Fig. 84 a comparison is made between the isotopic composition of crude oils from several analyzed deposits of the Permian Ural Area with their gas factor. There is no correlation, although a noticeable difference in the isotopic composition of petroleum and gas should have led to the enrichment in the heavy carbon isotope of the crudes that contain much gas if the latter actually came from petroleum. In addition, obviously there would have been an increased content of the heavy carbon isotope observed in the more ancient, more deeply buried crudes. Actually, the age dependence in the isotopic composition of crudes is absent, or, in any case, is not monotone.

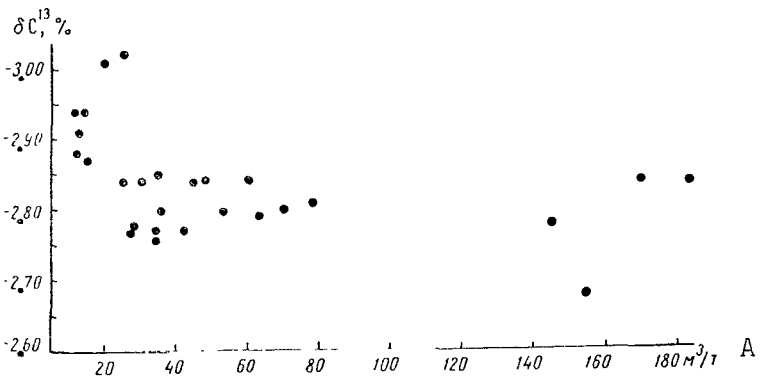

Fig. 84. Comparison of isotopic composition (percent) of carbon in crudes of the Permian Kama /sic/ Area with gas factor (m^3/ton)

KEY: A. m^3/ton

Thus, most of the gas is formed directly from the organic matter. At some stage methane is formed along with other hydrocarbons, that is, along with petroleum but not from it. However, in spite of the limited scale of the possible gas formation from petroleum, the presence of degradative processes culminating in the formation of methane is quite realistic, especially when petroleum has been deposited in deeply buried strata. Identification of methane of this origin could serve as an indicator of /306 the specific kind of geochemical processes occurring in the strata.

In this respect, it should be recalled that petroleum as a mechanical mixture of individual compounds must, in contrast to humified organic matter, experience in degradative processes the "normal" kinetic isotope effect. The isotope shift in methane formed during the cracking of petroleum is -2.5 percent at 500° C, while in methane obtained from the coalification of organic matter, $\Delta C^{13} = -0.7$ percent at 275° C. Therefore, under otherwise equal conditions the methane formed through the decomposition of petroleum hydrocarbons must be isotopically lighter (δC^{13} from -5.0 to -6.0 percent) than the methane formed at the mature stage of the transformation of organic matter (δC^{13} from -3.0 to -4.0 percent). This situation is reflected in Fig. 78 by section E.

An example of the realization of this process in natural conditions probably can be taken as the formation of by-product gases of crudes from deposits of the terrigenic Devonian of deposits in the Permian Ural Area.

Table 73 gives the typical values of the isotopic composition of individual hydrocarbons of by-product gases from crudes of the terrigenic Devonian (Pashiysko-Kynovskiye strata) and the Tul'sko-Bobrikovskiy (Yasnopolyanskiy) complex of the Lower Carboniferous.

TABLE 73. COMPARISON OF ISOTOPIC COMPOSITION OF BY-PRODUCT PETROLEUM GASES FROM SEVERAL YASNOPOLYANSKIYE (C_1jsp) AND PASHIYSKO-KYNOVSKIYE (D_3p + kn) POOLS IN THE PERMIAN URAL AREA

Deposit, borehole number	Depth, m	δC^{13}, ‰			
		CH_4	C_2H_6	C_3H_8	C_4H_{10}
Yasnopolyanskiye Deposits (C_1jsp)					
Chutyrskoye, 131	1279	—4.26	—3.22	—2.97	—2.65
Nozhovskoye, 8	1438	—4.94	—3.97	—3.26	—2.93
Kuz'minskoye, 85	1720	—4.84	—4.18	—3.26	—3.12
Aryazhskoye, 57	1388	—3.91	—3.89	—3.56	—3.14
Pashiysko-Kynovskiye Deposits (D_3p+kn)					
Tulvinskoye, 55	2108	—5.72	—4.30	—2.39	—3.15
» 68	2135	—5.43	—4.28	—2.37	—3.03
Kuliginskoye, 42	2305	—5.07	—4.33	—1.98	—2.84
» 42	2305	—4.86	—4.16	—2.18	—2.79

The fact that within the profile of one deposit or one geological region gases from the more deeply buried strata are considerably enriched in the light isotope compared with the overlying strata in itself is unusual and merits attention.

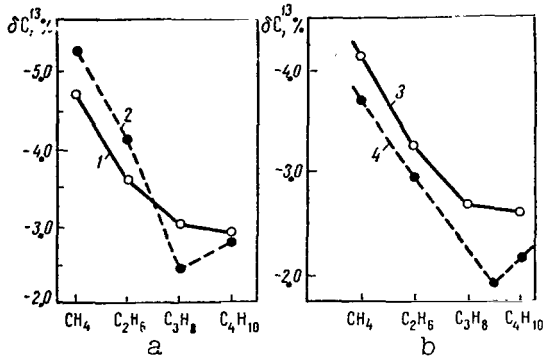

Fig. 85. Distribution of carbon isotopes in individual hydrocarbons of the Yasnopolyanskaya (1) and Devonian (2) crudes of the Permian Ural Area (a), in the initial gas-petroleum mixture (3) and in the gas-petroleum mixture (4) subjected to cracking at 500° C and a pressure of 200 kg/cm^2 (b)

By their content of C^{12} in methane ($\delta C^{13}_{av} = -5.3$ percent), by-products of Devonian crudes are at the level of the isotopically light gases from the early stage of the coalification of organic matter. At the same time, the formation of gases of this type from carbonized organic matter of the Devonian rocks, just like their incursion from the cover strata, considering the deep (more than 2000 m) burial of terrigenic Devonian would appear to be excluded. /307

As we can see from Table 73, by-products of Devonian crudes of the Permian Ural Area, besides the isotopically light methane, contain propane exhibiting "anomalous" isotopic composition. The latter is marked by a considerable enrichment in C^{13} and drops out of the successive isotopic series characteristic of methane homologs (Fig. 85, a). In this respect we should recall that in our experiments on the behavior of the petroleum-gas mixture at 500° C and at a pressure of 200 kg/cm^2, a substantial enrichment of propane in the heavy carbon isotope was also detected (Fig. 85, a), and see Table 62 for more details. The mechanism of this process is not entirely clear. Possibly, the cause of the anomalies is the breakdown of hydrocarbons containing four to five carbon atoms occurring under specific conditions. Here the methane and ethane formed are enriched in the light isotope, while there is the reverse accumulation of the heavy isotope in the rest of the molecule. In any case, there is an analogy between the abundance of isotopes in gaseous hydrocarbons of a petroleum-gas mixture subjected to cracking and by-product gases of the Devonian crude of the Permian Ural Area (of course we should consider that in nature the process takes place at much lower temperatures than laboratory cracking). There are grounds to maintain, thus, that these Devonian gases are the degradation product of crudes. In generalizing this phenomenon, we reach the conclusion that a distinguishing feature of gases formed through the transformation of crudes is that they contain isotopically extremely light methane and propane anomalously enriched in the heavy isotope.

Diffusional Fractionation of Carbon Isotopes in "Dry" and Water-Saturated Rock

The migration of gases in rocks not only leads to the redistribution of gases having different isotopic composition, but can also be the cause of specific isotope effects.

Mass appears in the expression for the diffusion coefficient. In particular, the diffusion rate of gas in a porous medium is proportional to the mean thermal rate

$$c_{av} = \sqrt{\frac{3RT}{m}},$$

therefore the diffusion coefficient of isotope separation is determined by the ratio of the square roots of the masses of the isotopic molecules:

$$\alpha = \frac{D_1}{D_2} = \sqrt{\frac{m_2}{m_1}}.$$

This ratio, which is ordinarily employed in various calculations, is sufficiently rigorous only for the case of self-diffusion and the diffusion of a gas through a "dry" porous medium not interacting with the gas. In natural conditions, the diffusional motion of gas always occurs in a wet medium. There are no "dry" porous media in sedimentary strata, with the exception of reservoirs containing gas pools or gas caps of oil deposits, although in this case the rocks contain considerable amounts of bound water. Gas molecules leaving a pool enter water-filled pores. Essentially, the mechanism of diffusional separation in this case is provided not by the porous character of the medium, but by the phenomenon of gas transport in a liquid.

The diffusion of gas in liquids in many respects differs from the diffusion of gas in gas or the so-called molecular escape of gas (through diaphragms, membranes, and porous media).

The diffusion coefficient D in a liquid is determined by the ratio

$$D = \frac{1}{6}\frac{\delta \bar{a}_v^2}{\tau},$$

where δ_{av} is the mean molecular distance, of the order of approximately $n \cdot 10^{-8}$ cm and defined by the ratio

$$\delta_{av} = \sqrt[3]{\frac{\mu}{N_0 \sigma}}$$

(μ is molecular weight, σ is density of liquid, and N_o is Avogadro's number); τ is the so-called relaxation time, exponentially dependent on temperature: /309

$$\tau = \tau_0 e^{\frac{\Delta W}{kT}}.$$

here τ_o is the period of vibration of a molecule about its equilibrium position in the liquid; ΔW is the energy of activation of the displacement of a molecule by the distance δ_{av}; and k is Boltzmann's constant.

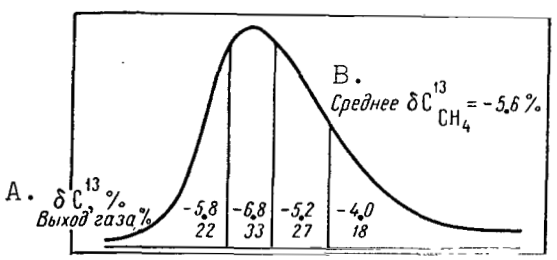

Fig. 86. Isotopic fractionation of methane as it is passed through a column filled with bentonite clay (helium is the carrier gas) /129/
KEY: A. Gas yield, percent
B. Mean

The variable τ_o is inversely proportional to the vibrational frequency, and the vibrational frequencies of the isotopic molecules are associated with the mass by the relation

$$\frac{\nu_1}{\nu_2} \approx \sqrt{\frac{m_2}{m_1}}.$$

Ultimately, the ratio of the diffusion coefficients are proportional to the square roots of the masses:

$$\frac{D_1}{D_2} \approx \sqrt{\frac{m_2}{m_1}},$$

but it is determined not by the mobilities (rates) of the isotopic species of the molecules, as in the case of gas diffusion, but by the vibrational frequencies of the molecules, which depend not only on mass. On being present in the liquid, gas molecules interact with it. In particular, solvation of methane molecules takes place in water. If this interaction is stronger for light molecules, the ratio of the diffusion coefficients can appreciably change -- to the extent that the transport rate of isotopically heavy gas molecules in a liquid can be higher than the transport rate of isotopically light molecules.

The possible role of diffusion in the isotopic fractionation of a gas has been studied most closely by the Italian workers U. Colombo, F. Gazzarrini, R. Gonfiantini et al. /135, 129/. On passing methane through a column filled with dry bentonite clay, the observed marked enrichment in the leading fractions with the light carbon isotope (Fig. 86). This gave them reason to involve the mechanism of the diffusional separation of isotopes to account for the correlations of the abundance of carbon isotopes in the gases of several gas deposits in Italy. It was found that here there is a successive change in the isotopic composition within a single pool from the basal section to the arch and in different gas horizons, upwards along the profile (Figs. 87 and 88). /311 /310

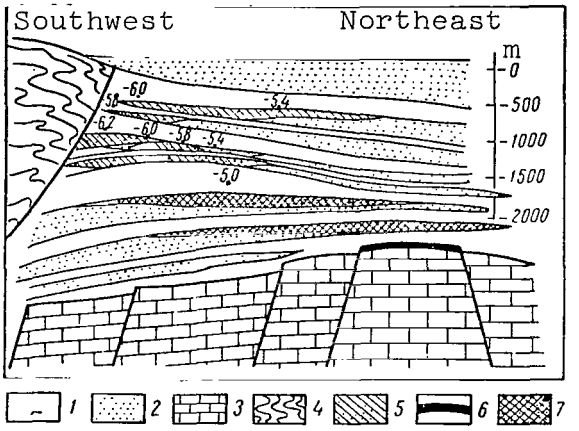

Fig. 87. Isotopic composition of methane from various sections of pool in Pliocene gas deposits of Southern Italy
1. Clay
2. Sand
3. Limestone
4. Flysch
5. Methane pools
6. Oil pools
7. Carbon dioxide with condensate /129/. The figures in the diagram are δC^{13} in percent

U. Colombo, F. Gazzarrini et al. /127/ were the first to point to the relationship existing between the isotopic composition of methane and the content in gas of heavier hydrocarbons (ethane and propane). As we can see in Fig. 89, plotted from the analysis of gases in Southern Italy, the higher the ethane concentration in the hydrocarbon portion of the gas, the isotopically heavier is the methane it contains -- -- exactly the same as in the bituminous gases of western regions of the FRG. By interpreting these functions together, the Italian investigators suggested that they are caused either by the mixing of isotopically light bacterial methane with petroleum gas containing heavier methane and higher hydrocarbons, or else by the diffusional effect of migration, during which the gas becomes depleted in the heavy hydrocarbons and simultaneously methane is enriched in the light isotope. Here, U. Colombo, F. Gazzarrini et al. recognized the more substantial role of the latter process.

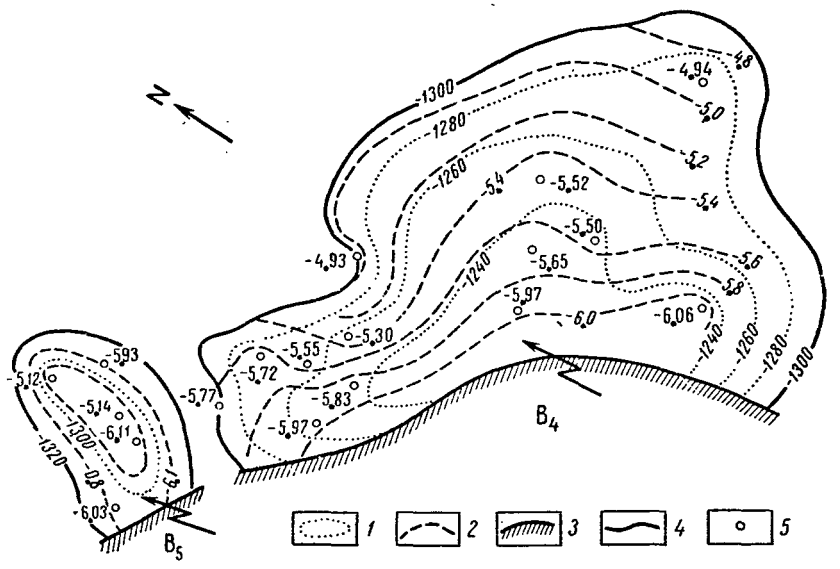

Fig. 88. Scheme of distribution of δC^{13} (in percent) of methane in the strata B_4 and B_5 in the Southern Italian gas field

1. Isobaths of stratal roof in m
2. Isolines of δC^{13} (in percent) of methane
3. Line of shielding disturbance
4. Contour of gas-bearing condition /129/
5. Wells

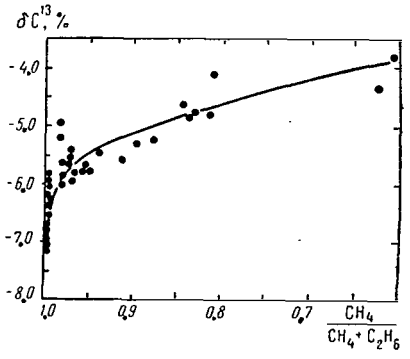

Fig. 89. Relationship of isotopic composition of methane with hydrocarbon composition of gas in Pliocene gas pools of Southern Italy /127/

The diffusional, or similar, separation of isotopes within a single gas reservoir is entirely possible. Other investigators have also noted the differentiation of carbon isotopes along the up-dip of a gas stratum. The Rumanian scientist, L. Blaga (oral communication), believes it is possible to account for this phenomenon by the presence of convective countercurrents of gas in the stratum, resulting in conditions for the thermal diffusional separation of isotopes.

W. Stahl /222/ observed the successive change in the isotopic composition of gas in the strata of the limestone Zollingen (West Germany) from $\delta C^{13} = -2{,}49$ percent at a depth of 2670 m to $\delta C^{13} = -2{,}66$ percent at a depth of 2190 m. He attempted to appraise the possible role of gravity differentiation of isotopes, using the barometric formula

$$\Delta C^{13} = \delta C^{13}_{CH_4 h} - \delta C^{13}_{CH_4 h=0} = \left[\left(1 + \frac{Gh}{T_0}\right)^{\frac{m_N g}{kG}} - 1\right] 100,$$

where h is the bedding depth of the gas measured from the arch of the reservoir horizon (h = 0); 1/G is the geothermal degree (m/°C); T_o is the temperature in the arch of the reservoir-stratum (K); m_N is the neutron mass (in other words, the difference in the masses of the molecules $C^{13}H_4$ and $C^{12}H_4$) (kg); g is the gravitational constant (m/sec^2); and k is Boltzmann's constant (J/°C). The value of the possible gravity differentiation thus calculated is about 0.03 percent per 100 m, in good agreement with the observed differentiation of isotopes in the sandstone Zollingen. /312

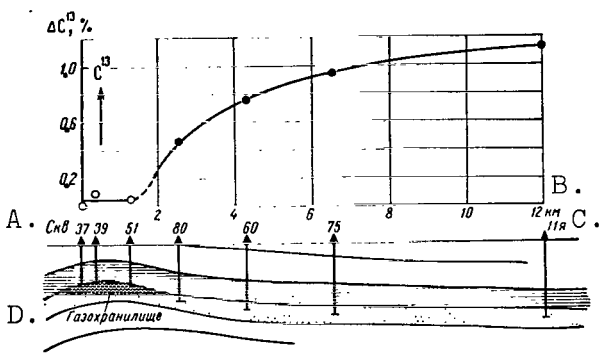

Fig. 90. Variation in isotopic composition of methane pumped in a gas reservoir and filtered through a reservoir-stratum, as a function of distance from pumping center (square 37)
KEY: A. Square
B. km
C. 11th
D. Gas reservoir

Thus, isotope separation within a gas pool evidently is accounted for by some form of the movement of gas in the reservoir (diffusional, convective, and gravitational) or their combination.

The separation of isotopes between different productive horizons separated by poorly permeable water-saturated strata is another matter. The migration of gas from one stratum to another in this case is associated with the diffusional penetration of gas through the liquid. Here the mechanism of isotope separation, as we noted earlier, can be entirely different than under gas diffusion.

For the first time the isotope effect for carbon in

methane as it is filtered through a wet medium was established in an investigation of the isotopic composition of methane samples from the dispersion aureole of a subsurface gas reservoir /27/. At the Kaluga gas reservoir, gas from the gas trunkline Dashava-Moscow terminates in the sandy stratum of the Gvodskiy horizon (Devonian), 800-900 m in depth. Pumping is carried out through compressor wells (Fig. 90, square 37). Squares 37, 39, and 51 are within the principal gas body of the reservoir; squares 80, 60, 75, and 11 are control squares and are located at different distances from the gas reservoir center. From these wells was removed gas saturated in stratal water, that had penetrated from a gas body through the Gvodskiy horizon. The isotopic composition of methane from all these wells was analyzed.

From the data, a graph was plotted (see Fig. 90) of the variation in the isotopic composition of gas (with respect to the /313 gas pumped into the compressor well) with increase in distance from the gas reservoir center. It was found that with increase in distance from the pumping site, methane carbon is enriched in C^{13}, that is, an effect opposite the one that could be anticipated from gas diffusion is present.

In the study cited, the hypothesis was advanced that the mechanism of isotope separation upon filtration through wet rock is caused by the predominant fixation (dissolving) of isotopically light methane, as the result of which isotopically heavy methane proves to be more mobile. A report on this effect at the Sixth Symposium on Stable Isotopes /152/ caused a discussion with Italian researchers F. Gazzarrini, R. Gonfiantini et al., who, by conducting his experiments in which they passed methane through dry bentonite, found, in contrast, enrichment of the leading portion of methane in C^{12}; accordingly, F. Gazzarrini in Italy set up a special experiment to determine the effect of water on the value and sign of the isotope effect of methane filtration. Methane was passed through a 13 m long tube filled with water. It was found that the leading portion of methane was actually enriched in C^{13}, confirming the results of the experiments with the gas reservoir and our own assumptions on the nature of the isotope effect observed.

In his address at the Amsterdam Congress on Organic Chemistry, F. Gazzarrini spoke as follows on this subject: "In our laboratory we carried out several kinetic experiments dissolving methane in water at low pressures and obtained data in agreement with the data of E. M. Galimov. The enrichment of $C^{13}H_4$ in the gaseous phase is due to the kinetic isotope effect caused by the higher rate of dissolution of $C^{12}H_4$. These experiments are, however,

of limited significance since the data obtained in equilibrium conditions more fully corresponds to geologic conditions. Our field observations are in full agreement with the suggestion by Meinshein that in nature $C^{12}H_4$ is more mobile than $C^{13}H_4$. Our interpretation, based on presently available information, is inclined toward the diffusional mechanism, but we cannot exclude the possibility that subsequent investigations on the equilibrium dissolution of isotopic species of methane can point to a certain contribution made by this mechanism to the complicated process associated with the migration of hydrocarbons" [129, p. 156].

Here it should be noted that the diffusional separation of isotopes also is kinetic in nature, therefore the problem of equilibrium applies (or does not apply) equally to both types of isotope effects examined. As for the field observations by the Italian investigators, as noted above, the diffusional mechanism can be related to the fractionation of isotopes within a given gas pool, but the variation in the isotopic composition of the gas in different productive horizons across the profile (increase in the content of the heavy isotope with depth) can be accounted for by other factors.

It is interesting to note that F. May and several other scientists of the GDR experimentally found the predominant adsorption of $C^{12}H_4$ in dry quartz sand, and on this basis also concluded that in nature there must be an outpacing migration of methane enriched in C^{13} [192]. P. Muller and R. Winholz [197], based on this effect, accounted for the enrichment in C^{13} of natural gas in Triassic deposits (Bundzondstein) of the Langelsalz Deposit by the migration of gas through a 300-meter stratum from lower-lying Permian deposits (Stasfurt carbonate). Even if this kind of isotope effect actually occurs in natural conditions, the preference must still be evidently given to the mechanism of methane enriched in C^{13} resulting from the dissolving of the gas in water, and not to its adsorption by dry rock.

Fractionation of Carbon Isotopes When Gas Dissolves in Water

In order to estimate the actual role of isotope effects associated with movement of gas in a water-saturated medium, we must establish the partition coefficient of isotopes in the system $CH_{4\,(gas)} - CH_{4\,(solution)}$. For this purpose, the experiment described below was undertaken in our laboratory.

In a system completely filled with water (Fig. 91), methane was introduced through stopcock 7 until it filled the volume V_o

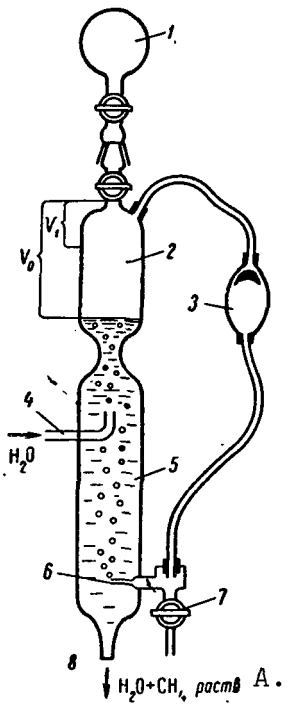

Fig. 91. Device for experimental determination of the fractionation coefficients of carbon isotopes in methane between methane in the gaseous phase and methane dissolved in water
1. Sampler
2. Gas collector
3. "Pear" rubber circulating pump
4. Inlet connecting piece for water
5. Column
6. Capillary for spraying methane into the column
7. Stopcock for introducing methane into the system
8. Overflow

KEY: A. dissolved

of the gas collector 2. Then the stopcock 7 was closed and water circulation was begun. Under a pressurehead, water was passed through connecting piece 4 and, on moving downward through the column, overflowed through arm 8. At the same time, methane was circulated by means of rubber pumps 3. Gas from the gas collector was repumped and sprayed through capillary 6 into column 5. Here the gas bubbles ascended counter /315 to the gas flow, and some of the gas dissolved and was entrained with the water through the discharge arm. As a result, the volume of the gas in the gas collector gradually decreased, reaching, after several hours of continuous pumping, some specific volume V_1.

The partition coefficient α corresponding to the isotope separation in the system $CH_{4\,(gas)}$ - $CH_{4\,(solution)}$ can be determined from the formula of Rayleigh depletion, which for this case is transformed as follows:

$$\alpha = 1 + \frac{\lg(1+\Delta C^{13}\cdot 10^{-2})}{\lg\frac{V_0}{V_1}}, \qquad \text{(VI.11)}$$

where ΔC^{13} is the difference in the isotopic composition -- measured on a mass spectrometer -- between the initial methane (occupying volume V_0) and the methane remaining in the gas collector (in volume V_1):

$$\Delta C^{13} = \delta C^{13}_{CH_4\,(1)} - \delta C^{13}_{CH_4\,(0)}.$$

TABLE 74. EXPERIMENTAL DETERMINATION OF PARTITION COEFFICIENTS OF CARBON ISOTOPES IN THE SYSTEM $CH_{4\,(gas)} - CH_{4\,(solution)}$

$\frac{V_2}{V_1}$	ΔC^{13}, %	α
1.25	0.01	1.0004
4	+0.03	1.00026
20	+0.11	1.0003
1000	+0.19	1.0003

The experimental results are in Table 74.

From Table 74 it above all follows that methane in the gaseous phase ($CH_{4\,(gas)}$) is enriched in C^{13} compared with the methane dissolved in water ($CH_{4\,(solution)}$); this confirms the above observations.

The partition coefficients of isotopes α accompanying processes of the developing of methane in water and its release from water into the free phase proved to be 1.0003. It corresponds to the isotopic shift in gaseous methane $\Delta C^{13} = +0.03$ percent.

Let us examine the possible role of effects of this kind in natural conditions with the example of the following model (Fig. 92). Suppose methane from a gas pool in stratum I or methane generated in the gas-parental strata Ia enters reservoir II, where stratal waters are in movement. Some of the methane here dissolves and is swept away from the area that is gas collecting for the given trap. The remaining methane accumulates at the base of the cover II. Let us assume that the permeability of cover IIa is smaller than Ia. Otherwise, the accumulation of gas would not occur. /316

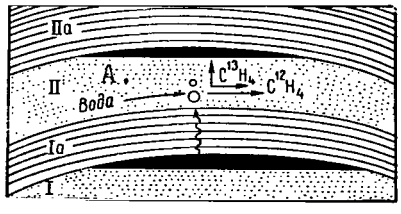

Fig. 92. Scheme of separation of carbon isotopes in methane in vertical migration I, Ia, II, IIa. Strata
KEY: A. Water

The amount of dissolved gas transported into stratum II by a single column of water of thickness H per unit of time is $vH\gamma$, where v is the flow rate of the water and γ is the solubility of methane in water under the given conditions. The amount of methane entering this unit column, that is, generated per unit time per unit area of the roof of stratum Ia, we will denote with q.

By solving Eq. (VI.11) for ΔC^{13} and taking note of the fact that in this case $V_o = q$, and $V_1 = V_o - vH\gamma$, we get:

$$\Delta C^{13} = 10^2 \left[\left(1 - \frac{vH\gamma}{q} \right)^{\frac{1-\alpha}{\alpha}} - 1 \right]. \qquad \text{(VI.12)}$$

If the flowrate of water is high, that is, $vH\gamma \gg q$, all of the released methane will be virtually dissolved and swept away from the gas collecting zone. Formation of the pool in stratum II will not occur.

If the flowrate of the water is very low, that is, $vH\gamma \ll q$, then after a specific amount of time it will be saturated with methane. Further penetration of the gas through the strata of reservoir II will not be accompanied by an isotope effect. In this case the isotope composition of the gas in the pool formed in stratum II and the gas entering from low-lying deposits will be virtually the same (if we neglect the difference caused by the residence of some of the gas in the dissolved state in the water). This distinction is virtually undetectable because of the mass of the gas in the pool is considerably greater than the mass of the gas dissolved in water.

From the point of view of the possible fractionation of isotopes, only the case when the flowrate of water and the gas generation rate are comparable is of interest.

In the gases of the Permian Ural Area analyzed, methane in the Tournaisian deposits is enriched approximately 0.2 percent relative to the methane in the lower-lying Devonian deposits. It can be calculated under which conditions this enrichment will occur due to the isotope effect we are considering if we bear in mind the vertical migration of gas from the Devonian. Assuming the flowrate of the stratal waters to be approximately 10 cm/sec, the thickness of the deposits between the productive horizons /317 of the Devonian and the Tournaisian is about 100 m; the solubility of methane in water is approximately 10^{-4} g/g; and the partition coefficient $\alpha = 1.0003$; we get the hydrocarbon flow $q = 5 \cdot 10^{-8}$ g/cm^2. However, here it turns out that less than 1 percent of the gas migration from the Devonian reaches the traps in the Tournaisian deposits.

Clearly, vertical migration can be efficient (in the sense of its role in pool formation) only for a much higher intensity of flow. But this means a corresponding reduction in the isotopic shifts. Therefore, in neither the case of gases from the Permian Ural Area, or in the more general case -- within the model we are considering -- can the isotope effect associated with the predominant dissolution of isotopically light methane in water evidently have a strong affect on the abundance of carbon isotopes in gases.

Fractionation of Carbon Isotopes During the Degassing of Petroleum

In natural conditions, petroleum along with the gas dissolved in it is a highly mobile system. When the stratal pressure is increased or the temperature is decreased during geologic history, some of the gas can enter the free state and with time leave the pool through diffusional dispersion. In contrast, if the stratal pressure exceeds the petroleum saturation pressure, it can dissolve additional portions of gaseous hydrocarbons reaching the trap. Therefore it is very important to know whether processes of the dissolving of gas in petroleum and the degassing of petroleum are accompanied by any isotope effects.

For this purpose, an experiment on differential degassing of petroleum was set up. Petroleum with its dissolved gas in a standard sampler was placed in a device for contact degassing. The pressure in the container (sampler), initially kept at 150 kg/cm^2, was reduced somewhat below the saturation pressure, which for the petroleum sample analyzed was 89 kg/cm^2. The hydrocarbons liberated into the gaseous phase were separated with a chromatographic column into individual hydrocarbons, and their isotopic composition was analyzed. The volume of the initially released gas was about 5 percent of the total amount of gas dissolved in the petroleum. Then the container pressure was lowered to 5 kg/cm^2. Here most of the dissolved gas was liberated. Finally, when the pressure was brought to the atmospheric, the tail sample of the dissolved gas was collected, amounting in volume, just as the initial sample, to about 5-6 percent of the total volume of the gas in the petroleum.

As Table 75 shows, no systematic variation in the isotopic composition of hydrocarbons liberated at different stages of degassing occurred, although for methane we can note a small enrichment in C^{13} (by 0.04 percent) in the part of the gas liberated in the last portion. /318

TABLE 75. RESULTS OF EXPERIMENT ON DIFFERENTIAL DEGASSING OF PETROLEUM (SATURATION PRESSURE 89 kg/cm^2)

Hydrocarbons analyzed	δC^{13}, %		
	89-85 kg/cm^2	85-5 kg/cm^2	5-1 kg/cm^2
CH_4	−4.14	−4.12	−4.10
C_2H_6	−3.22	−3.17	−3.23
C_3H_8	−2.70	−2.67	−2.71
C_4H_{10}	−2.63	−2.61	−2.61

The experiment was conducted so that the thermodynamic phase equilibrium was not reached and these results reflect not the separation of isotopes in the system $CH_{4(gas)} - CH_{4(solution)}$ or $C_2H_{6(gas)} - C_2H_{6(solution)}$, and so on, but the isotope effect of removing gas from the surface of the liquid phase.

The experimental results afford grounds for assuming that in natural conditions as well, similar isotope effects are slight.

Separation of Carbon Isotopes in the System Free Gas -- -- Adsorbed Gas

Bituminous gas is usually subdivided into two categories: free gas forming gas accumulations in the strata of bituminous coal, and adsorbed gas bound to the coal by surface forces. Free gas is given off by the simple crushing of coal, and adsorbed gas -- usually by heating ($T \approx 120^{\circ}$ C) crushed coal in a mixture with quartz sand in vacuum. The proportion of adsorbed gas is 60-90 percent of all the gas present in bituminous coal. Its composition usually has much more of the heavy homologs of methane than does the free gas.

A comparative study of the isotopic composition of free and adsorbed methane showed that the latter is considerably enriched in the heavy carbon isotope. In coals from the Vorkuta Basin, this enrichment is 0.02-0.1 percent /28/, in coals of the Ruhr Basin -- 0.01-1.0 percent /128/, and in coals of the Donbass -- -- more than 1 percent /76/. Thus, stable enrichment of adsorbed methane in C^{13} is observed, averaging approximately 0.5 percent.

Available data show that the size of the isotope effect, /319
that is, the difference between the isotopic composition of adsorbed and free methane, is independent of the methane content in coal (Fig. 93 a), or the ethane content (Fig. 93 c) as well as the ratio of the ethane concentrations in adsorbed and free gas (Fig. 93 b), that is, in dependent of the parameters characterizing the intensity of the gas formation and generation of heavy hydrocarbons, respectively, and the "surface activity" of coal. There is also no relationship between the age and degree of metamorphism of coal. Thus, there are no functions that could serve as a key to understanding the nature of the isotope effect observed.

Supposedly, the depletion of adsorbed methane in C^{12} can be attributed to the desorption effect. From the kinetic point of view, the hypothesis that follows is entirely applicable: the

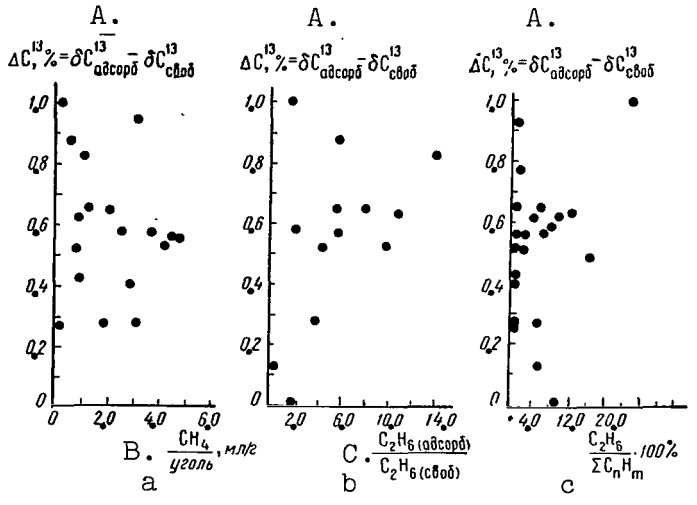

Fig. 93. Comparison of δC^{13} values characterizing the difference in the isotopic composition of carbon in adsorbed and in free methane with the concentration of the sorbed methane in coal (a), ratio of the concentrations of adsorbed and free ethane (b), and the relative content of ethane in free gas (c).

KEY: A. $\delta C^{13}_{adsorb} - C^{13}_{free}$

B. CH_4/coal, ml/g

C. $\frac{C_2H_6\ (adsorb)}{C_2H_6\ (free)}$

passage of methane from the active surface of the coal into the free phase is completed with some preference for $C^{12}H_4$ over $C^{13}H_4$. But it must be borne in mind that in the reverse process of adsorption, isotopically light methane has the same kinetic advantages, therefore the isotope effect of desorption must virtually be entirely removed by exchange. Only when the gas is rapidly removed from coal is a marked manifestation of the desorption effect possible. In geologic conditions the rate of gas release obviously is much lower than the rate of the adsorption-desorption exchange.

Isotope Effect When Carbon is Regenerated in the Solid Phase from Gas /320

To explain the difference in the isotope composition of free and adsorbed coal methane, as well as several other cases in which coal and ethane is enriched in the heavy isotope, we can turn to the mechanism of the heterogeneous isotope effect we detected in the system C - CH_4 [31, 93]. Recall that this effect was observed in the synthesis of diamond and graphite from methane, where the diamond was enriched in the experiments approximately by 2.5 percent in C^{13}, and the graphite (carbon black carbon) -- -- by 2.0-2.5 percent in C^{12} relative to the initial methane.

When solid carbon was grown from methane carbon, if the mass of the carbon in the gaseous phase was commensurable with the mass of the methane regenerated in the coal, the methane carbon can be considerably depleted in C^{12} through the above-mentioned heterogeneous isotope effect. The basis of this method presents no difficulties from the quantitative point of view. But in this

case we have to assume that in the coalification process not only is methane generated, but also the reverse process of the deposition of methane carbon in coal. However, there is nothing in this assumption that would contradict established facts. Rather, the opposite is true. We know that methane rapidly exchanges its carbon with coal, which then signifies in the forward process the passage of methane into coal.

M. B. Neyman /85/ studied the exchange of CH_4 and CO with coal, using the C^{14} radioisotope. When $C^{14}O$ was introduced into a reaction vessel containing carbon black, the specific activity of the carbon after a 2-hour exposure was 0.068 microcurie/millimole, and after a 4-hour exposure it climbed to 0.1 microcurie/millimole (for the initial specific activity of CO - 7.2 microcurie/millimole), indicating the quite rapid exchange in the reaction $C^{14}O + C \rightarrow C^{14} + CO$. Similarly, it was shown that exchange is present in the reaction $C^{14} + CH_4 \rightarrow C^{14}H_4 + C$. Thus, the chemical "growth" of coal from methane carbon is entirely possible.

In natural conditions the regeneration of the solid phase of carbon from the gaseous occurs in the formation of graphite pseudomorphisms. Probably, some role in this process is played by the fossil plant remains completely replaced with carbon, as well as in the formation of structureless ingredients of bituminous coals.

Thus, enrichment in C^{13} of the adsorbed methane and formation of methane that is isotopically heavier than the initial coal (for example, in several anthracites) can at least in part be regarded as resulting from the chemical transition of some of the adsorbed methane into coal. Through the heterogeneous isotope effect in the C - CH_4 system, which as was shown above leads to the concentration of C^{12} in the solid phase, the methane remaining in the adsorbed state is enriched in C^{13}. Of course, we must not overstate the geologic significance of the process /321 in which the solid phase is regenerated from gas: we can discuss only some spatial redistribution of coal carbon and an increase in the degree of its homogenization.

Dissipative Fractionation of Isotopes

Gases undergo continuous dispersion in sedimentary rocks. It is important to note to what extent this process can influence the isotopic composition of gas remaining in pools. Solving this problem in general form by relying on the diffusion equation requires that we know several parameters, which are not easy to estimate and involve cumbersome manipulations. However, the necessity for

this disappears if we accept as plausible the assumption that the generation rate of gas in sedimentary rocks is equal to the rate of its dispersion, that is, during specific intervals of geologic time the mean content of gas in the sedimentary profile is retained at the more or less constant level.

Thus, as can be readily observed, this process becomes analogous to the process of the fractional "distillation at a constant level", for which we have the equation

$$\ln \frac{\alpha-1}{\alpha-N/N_0}=\frac{V}{\alpha V_0},$$

where V_0 is the content of gas in the sedimentary profile; V is the total amount of generated (dispersed) gas in the calculated time interval; α is the partition coefficient of the isotope; and N/N_0 is the ratio of the isotopic compositions of the gas at the calculated moment and of the initial gas, which then is the isotopic shift ΔC^{13}.

An important property of this expression is that the isotopic shift cannot exceed the partition coefficient of the isotopes and at the limit (as $V \to \infty$) tends toward it. Thus, using the above-presented equation we can, independently of the actual mechanism of the process, the gradient of the distribution of isotopes across the profile, the concentrations of gases, and the rates of their formation and flow, estimate the maximum possible isotopic shift in a gas resulting from the dissipative process if we know the partition coefficient of the isotopes in the elementary process.

Since the dispersion process is diffusional, obviously we must take as the partition coefficient the value of α, characterizing the diffusion of gas in natural conditions. In practice this quantity cannot be measured.

If it is assumed that the fractionation of isotopes during dispersion is similar in character to the separation of isotopes when methane is removed with water (as in the above-described experiment), the corresponding $\alpha = 1.0003$. In this case the resultant isotopic shift of the steady-state dissipative process /322 is only 0.03 percent. If we base our approach on the "dry diffusion" and take $\alpha = 0.997$ corresponding to the isotopic shift of methane when it is passed through dry bentonite, in accordance with the foregoing, the maximum enrichment of methane in the heavy isotope that is due to its dissipation will not exceed + 0.3 percent.

Thus, the variation in the isotopic composition of gas in a pool resulting from the steady-state dissipative process is small.

Estimation of the Conditions for Formation and Migration of Gases from Isotopic Composition

Principles of Genetical Classification of Gases

The above data suggests the conclusion that isotope effects caused by migration (diffusion, dissolving in water, and degassing) are small compared with the isotopic shifts caused by genetical factors. This narrows the possibilities of the direct use of isotope effects, for example, in estimating the direction of migration. But, on the other hand, it is precisely the smallness of the isotope effects associated with the movement of gases that makes it possible to broadly use isotopic information for the genetical identification of gases, and this means, also to judge the presence and nature of migration.

Fig. 94 shows a scheme of the abundance of the isotopes of methane carbon in gases of different origins. In many cases the ranges of variation in δC^{13} of methane overlap. However, from the mechanism of methane formation, we can bring into consideration additional features, which taken together with the data on the isotopic composition of methane can aid us in more exactly establishing the genesis of the gas. Gases of microbiological origin (region I of the abundance of the isotopic composition of methane) are difficult to distinguish from gases forming through the chemical degradation of weakly altered organic matter (in region II). In both cases the gases contain isotopically extremely light methane. The higher homologs of methane are absent. However, in the isotopic shift caused by the activity of bacteria is virtually independent of the condition of the initial substrate, therefore isotopically light methane of biological origin can be generated in rocks containing strongly coalified matter. This situation arises when ancient deposits outcrop. Examples of this type were considered above. We must also include in the category of biochemical gases those containing methane especially enriched in C^{12} ($\delta C^{13} = -7.0$ percent and smaller).

Depending on the stage of coalification with which the degree of intramolecular nonuniformity of the organic matter is associated, methane of extremely diverse isotopic composition can be formed: from the isotopically lightest (region II) to the isotopically heaviest (region VI). /323

Enrichment in the heavy carbon isotope of methane formed at the mature stage of the catagenesis of organic matter is due to the involvement of the radical mechanism. The radical-conjugate character of the reactions is intrinsic to the petroleum-forming process, therefore isotopically heavy methane in

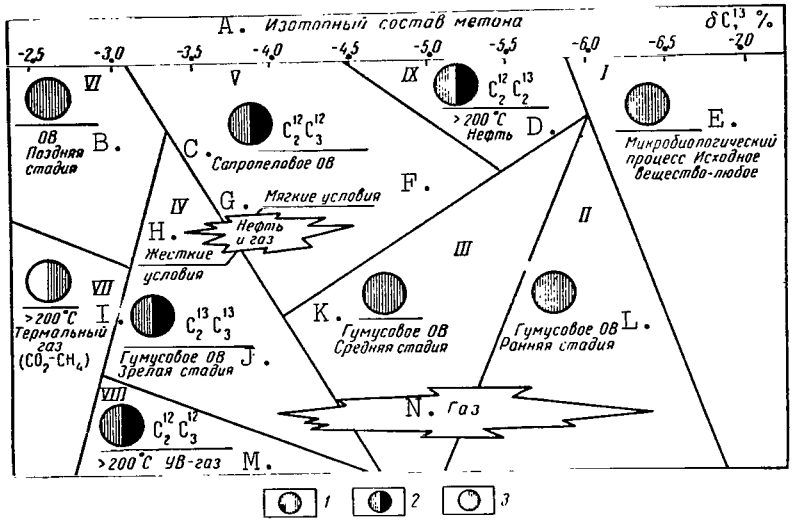

Fig. 94. Scheme of genetical identification of gas from the data of its isotopic and chemical composition (I-IX. Regions corresponding to different genetical categories of gas)

1. $CH_4 \geqslant 90$ percent
2. $C_2-C_4 \geqslant 10$ percent
3. $CO_2 \geqslant 50$ percent
4. C_2^{12} and C_2^{13}, C_3^{12} and C_3^{13} stand for the relative enrichment in the light or heavy carbon isotope of ethane and propane, respectively

KEY:
- A. Isotopic composition of methane
- B. Organic matter, late stage
- C. Sapropelic organic matter
- D. Petroleum
- E. Microbiological process, any initial material
- F. Mild conditions
- G. Petroleum and gas
- H. Severe conditions
- I. Thermal gas
- J. Humus organic matter, mature stage
- K. Humus organic matter, middle stage
- L. Humus organic matter, early stage
- M. Hydrocarbon-gas
- N. Gas

this case is obtained along with higher-molecular hydrocarbons. This methane can be regarded as syngenetic to petroleum. Carbon isotopes in ethane, propane, and butane are distributed in the normal sequence. It can only be expected that hydrocarbons of the earlier stage of the process will, on the average, be isotopically lighter. Therefore ethane and propane generated by organic matter of the sapropelic type (region V) must be somewhat richer in C^{12} than the same hydrocarbons generated by organic matter of the humus type (region IV) for which the stage /324
of development of the radical reactions sets in somewhat later -- -- at a higher stage of maturity than for the lipid-enriched sapropels. In Fig. 94, this is reflected in the formulas of the distribution of carbon isotopes in ethane and propane -- -- $C_2^{12}C_3^{12}$ (category V) and $C_2^{13}C_3^{13}$ (category IV).

If we concentrate our attention not on the kind of organic matter, but on the conditions of its transformation, it can be stated that gases relating to category V are formed in milder temperature conditions than category IV gases.

Isotopically light methane is obtained through the degradation of petroleum hydrocarbons (region IX). This process is realized if the petroleum pool is subjected to thermal metamorphism. The cause of the high isotopic shifts in this case is the kinetic isotope effect. Petroleum hydrocarbons in contrast to organic matter exhibiting polymeric structure form products of dissociative reactions with a "normal" kinetic isotope effect. Gas of this origin, in contrast to other isotopically light gases, contains high-molecular hydrocarbons characterized by an additional feature -- heavy isotope-enrichment of propane (the distribution formula of $C_2^{12}C_3^{13}$). The latter differentiates this gas from hydrocarbon gases generated by sapropelic organic matter at an early stage of coalification (region V).

Methane genetically associated with coals having a high degree of metamorphism (anthracite stage) is enriched in the heavy isotope through the attainment by the organic matter of isotopic univormity (the isotopic shift caused by the intramolecular distribution of isotopes is brought to zero), and also due to the low values of the kinetic isotope effects caused by the mechanism of gas separation "layer by layer." Gas of this origin (region VI), in contrast to isotopically heavy methane syngenetic with petroleum is depleted in the higher homologs.

Methane relating to thermal gases (region VII) is enriched in the heavy isotope through postgenetical processes. Its isotopic

composition is caused by exchange in the system CO_2 - CH_4. Initially, this methane could have been of any origin and of any isotopic composition. At the isotopic composition of CO_2 estimated on the average by $\delta C^{13} = -0{,}7$ percent, in conditions of equilibrium exchange at temperatures greater than 200° C, methane acquires the isotopic composition characterized by $\delta C^{13} = -2{,}5$ percent. In order for the secondary thermodynamic isotope effect to substantially affect the isotopic composition of methane, a large amount of carbon dioxide is needed. Therefore methane whose enrichment in the heavy carbon isotope is due to exchange in thermal conditions must be marked by the presence in the gas composition of a considerable amount of carbon dioxide.

Hydrocarbons of a gas pool subjected to thermal metamorphism (region VIII) must have a distinctive isotopic composition. As a result of the isotopic exchange in the system CH_4—C_2H_6—C_3H_8—C_4H_{10}, which at temperatures of 150-200° C is completed in a geologically short time, the isotopic composition of all hydrocarbons will prove to be closer together. Controlling will be the isotopic composition of the most abundant homologs. In particular, if the gas has a predominance of methane, formation of isotopically extremely light ethane and propane ($C_2^{12}C_3^{12}$) is possible. /325

This scheme of the abundance of δC^{13} of methane in gases of different genesis (see Fig. 94) is a kind of graphical overlay that can be used for the genetical identification of a gas. Let us assume, for example, that analysis of the isotopic composition of a methane gave $\delta C^{13} = -5{,}0$ percent. This methane may have been formed from organic matter of the humus type at the middle stage of its coalification (region III), from sapropelic organic matter of an earlier stage of coalification (V), or through the thermal degradation of petroleum hydrocarbons (IX).

Further, we must turn to the hydrocarbon composition of the gas. If in the gas ethane and other higher-molecular hydrocarbons are absent or if their content is low, we can conclude that the gas originated via (III), but if the content of these hydrocarbons is considerable ($\geqslant$ 10 percent), preference must be given to the cases (V) and (IX). In order in turn to single out one of the latter, we must analyze the isotopic composition of ethane and propane. As we can see from the graphic overlay for a gas formed from the thermal metamorphosis of an oil pool or bitumenous shales, isotopically heavy propane is characteristic.

These cases of course far from exhaust the full diversity of geologic situations. But overall, obviously one can agree that isotopic data makes it possible to obtain definite information about the origin of gases if one starts from an understanding of the causes and mechanisms underlying the formation of the isotopic composition of the gas.

It should be stressed that since the isotopic composition of a gas is controlled above all by primary (genetical) factors, with a much smaller role for such secondary factors as interaction (exchange) with the environment or bedding conditions, it is proper to pose the question specifically of the genetical, and not the morphological identification of gases. With access to the isotopic analysis of a gas sample, one cannot in the general case determine to which type of pool this gas belongs (gas, oil-gas, or oil), and in what state it exists -- dissolved or free.

As we can see from Fig. 64, the ranges of variation in the isotopic composition of methane in morphologically diverse gases is combined to a large extent. It is easy to cite specific examples. Thus, methane from the gas pools in Southern Italy have δC^{13} from -5.5 to -6.5 percent, while methane from gas pools in the northwest regions of the FRG are characterized on the average by $\delta C^{13} = -2,5$ percent. Similarly, methane present in by-product gas just in the oil pools we investigated in the Permian Ural Area have an isotopic composition varying from -3.2 to -5.8 percent. Accordingly, we cannot but note that the somewhat simplified approach of certain investigators, for example, F. A. Alekseyev who recommend the isotopic analysis of methane as a criterion for classifying gas, oil-gas, and oil pools is fraught with errors. /326

Determination of Migratory Origin of Gases

Gases dissimilar in conditions of formation (and thus, distinct in isotopic composition) can belong to the same morphological type. Also no less central is the fact that hydrocarbons of petroleum and gas forming together can become separated during geologic history.

Through migratory and dissipative processes the oil pool can lose the primary gas genetically associated with the petroleum (having an isotopically heavy methane intrinsic to the petroleum-forming process), and acquire gas having a different origin, for example, with the isotopically light methane of the early stage of the metamorphism of organic matter.

What was said in the previous chapter about the role of the seismic factor in the mechanism of hydrocarbon migration and accumulation, plus the concept deriving in particular from isotopic data that dissipative processes have a large role enables us to outline the following essential types of the spatial differentiation of petroleum and gas:

1) the genetic type caused by the fact that depending on the stage of metamorphism of the organic matter and the external conditions, the stages of the predominant petroleum formation and gas formation are displaced in time;

2) emigratory type caused by the fact that the primary migration and accumulation of gases requires less stringent conditions of seismicity, owing to which with the development of a basin in a relatively quiet tectonic environment, the accumulation of hydrocarbons can be limited to the formation only of gas pools;

3) the migratory type, associated with the difference between the physical properties of petroleum in gas, which during migration lead to the separation of phases, in particular, based on the Maksimov-Gassou principle of differential trapping; and

4) dissipative type, caused by the different rate of dispersion of liquid and gaseous hydrocarbons, which in the case of a primordially oil-gas pool sooner or later leads (depending on the properties of the covers or, using a more general term suggested by Roberts, on the competence of the traps) to the total loss of the gas phase and the formation of residual oil pools.

Through the essentially different diffusional mobility of gaseous hydrocarbons and high-molecular hydrocarbons of petroleum, /327 petroleum can be kept in a reservoir for a protracted geologic time, while the gas will relatively rapidly be lost. From the results of a calculation based on the rate of diffusional dispersion of gases and also an isotopic analysis of gas carbon, most of the gas formed in Prepaleogenic time probably will have been lost by the sedimentary rocks. In other words, nonsyngenetic gas, but gas regenerated at a later time will accompany ancient crude oils, for example, of Paleozoic age. Hence it follows that only oil-gas provinces confined to seismically active zones of juvenile folding or the most Recent shoves of the basement can contain syngenetic pools of petroleum and gas. Oil-bearing basins of ancient platforms, in which the time of oil-gas accumulation is associated with early tectogenesis, will contain only oil deposits or gas accumulations resulting from the accumulation of a later process of gas formation. This possibly accounts for the different distribution of oil and gas deposits in juvenile and ancient platforms: the increase in gas presence from the marginal trough to the platform in the former, and the decrease in gas presence in this direction -- in the latter.

The above-examined genetical scheme of gas formation brings into direct correspondence their isotopic composition with the

nature of the initial material, the degree of its transformation, and the conditions of gas generation. However, the picture to a large extent is complicated by subsequent migratory and dissipative phenomena. As a result, the gases may be in situations differing widely from the environment of their formation and as a consequence their isotopic composition will be in contrast to the characteristics of the intervening deposits. It is precisely this state of contrast that can serve as a basis for judging the migration of a gas.

Methane enriched in the light carbon isotope is generated in the upper zone of sedimentary rocks. The appearance of isotopically heavy methane in the surface deposits could testify to productive horizons present at great depths. However, this feature should not be given special weight. In order for a well-defined shift in the isotopic composition of a gas in covered deposits to have arisen, the inflow of isotopically heavy methane from the deep interior should be so considerable that the pool would have been exhausted in a geologically short time.

The distance in isotopic composition of surface gases and gases of deeper bedding can be more successfully employed for technical purposes, for example, for monitoring the hermeticity of the covers of subsurface gas reservoirs. Together with V. N. Dakhnov we developed a method of detecting leaks from gas reservoirs, which can be seen in its essentials from the following example of its use.

At the Kolpinskoye gas reservoir, after a trial pumping gas manifestations were found in Quaternary covered deposits. The trap of the gas reservoir here was a sandy stratum, more properly, three strata of Gdovskiy horizons bedded at 270-290 m. /328
It was necessary to find whether these gas manifestations were the consequence of the flow of gas from the trap-stratum or else natural gas generated directly in the Quaternary deposits. As we know, when there is a small leak it is not always possible to find whether the gas recorded in the monitoring wells is of local origin or whether it has come from the gas reservoir. Sometimes in these cases one resorts to radioactive isotopes, that is, to the labeled atom method. This method gives reliable results, but it has substantial drawbacks: it is required to pump into the stratum in large amounts an expensive radioactive preparation; the use of radioactive isotopes proves to be undesirable from sanitary-hygienic considerations. The isotopic composition of methane from the cover depsoits was -4.08 percent, which is far beyond the limits of δC^{13}, values characterizing methane syngenetic to the cover deposits (δC^{13} from -5.0 to -7.5 percent). The productive horizons of large oil-gas deposits supply natural gas to industrial centers, that is, the gas that is pumped into underground gas reservoirs lies as a rule considerably deeper than

500 m, and the methane therein has δC^{13} from -3.4 to -5.0 percent, with a mean of -4.2 percent. Control analysis of the gas from the gas reservoir gave $\delta C^{13} = -4{,}19$ percent for the isotopic composition of methane. As a result, it was concluded that the gas in the gas manifestations investigated was of allochthonous origin and that it had leaked from the gas reservoir.

Detection of isotopically heavy methane in deposits where organic matter corresponds to a relatively low degree of coalification can indicate the migratory origin of this gas. Gas with this isotopic composition can be genetically associated with the crudes, with coals of a high degree of metamorphism, or else this gas may be a thermal gas. Using the graphic overlay (see Fig. 94), one can make a more detailed distribution. Gas syngenetic with petroleum contains in addition to heavy isotope-enriched methane an increased amount of ethane and propane. Gas genetically associated with coals having a high degree of metamorphism (anthracite stage) is characterized by isotopically heavy methane, but is depleted in its higher homologs. Thermal gases are enriched in carbon dioxide.

On finding the genesis of a gas, one can by reckoning with the geologic structure of the region and the facial composition of the deposits indicate its specific source, therefore, to a large extent determine the direction, and sometimes the time of migration.

Detection of isotopically light gas in deposits where the organic matter is at a relatively late stage of coalification can testify to the existence of lateral migration from a zone where the organic matter had been subjected to less prolonged and less intensive metamorphism, if of course this assumption is admissible from geologic considerations. /329

Isotopically light methane can be formed in rocks containing deeply metamorphized organic matter if these rocks are found to be upthrust and are characterized by relatively open hydrodynamic conditions. In this case the gas source can be not the coalified remnants of the organic matter in the rocks, but by the less altered constituents of "juvenile" organic matter arriving with stratal water. If these rocks lie at a depth attainable for microflora regardless of the nature of the initial carbon, isotopically light methane of biochemical origin is formed.

Isotopically, relatively light methane is obtained through the degradation of petroleum hydrocarbons. Methane, being a product of the transformation of petroleum, plays a minor role in the general balance of gas. But the detection of this methane can serve as an indication that oil pools are present in deeply buried deposits. In contrast to other isotopically light gases,

a gas of this origin contains much ethane and propane. Evidently, a characteristic property of gas formed as a product of natural cracking of crudes is also an anomalous enrichment of propane in C^{13}. We can encounter propane that is isotopically heavier than butane and heavier than petroleum hydrocarbons overall.

In addition to petroleum, gas containing isotopically light methane, with analogous characteristics of content and isotopic composition of ethane, propane, and butane, can be generated by bitumenous shales in the same conditions in which the natural cracking of crudes takes place.

Distribution of Carbon Isotopes in Gases Over the Area of the Oil-Gas Province. The Construction of Processes of Pool Formation in the Permian Ural Area

Fig. 95 gives insert tables containing the characteristics of by-product gases from petroleum deposits in the Permian Ural Area, set up in accordance with the location of these deposits in this territory. The scheme was compiled for gases of the Yasnopolyanian Substage from the results of analyses included in Table 6, to which the reader must turn for additional information.

Now let us look first at the δC^{13}, values characterizing the isotopic composition of methane. We cannot detect any correlation in the distribution, areally, of these quantities taken separately. For the Yasnopolyanskiye crudes of Permskaya Oblast, as was shown in Chapter Four, there is a well-defined differentiation in the northwest field in the abundance of isotopically light crudes, and in the southeast field -- in isotopically heavy cruces with a boundary running approximately along the /331
southern margin of the Kamsko-Kinel'skaya system of troughs (see Figs. 33 and 34). In this case there are isotopically light and isotopically heavy gases (with respect to methane) in both parts of the oblast. In the region of the Cis-Ural trough, for example, there are also gases containing both isotopically light methane (Ol'khovskoye Deposits, $\delta C^{13} = -5{,}18$ percent), as well as isotopically heavy methane (Brusnyanskoye Deposits, $\delta C^{13} = -4{,}09$ percent).

Now let us try to interpret the isotopic data by relying on the genetical scheme presented in Fig. 94. Ol'khovskaya petroleum contains a gas which by the isotopic composition of methane ($\delta C^{13} = -5{,}18$ percent) can be classed in the genetical category IX, V, or III. From Table 60 it is clear that the C_2 - C_4 hydrocarbons are abundantly represented in the gas composition. Therefore, the variation in the genetical origin of a gas must be narrowed to the categories IX and V.

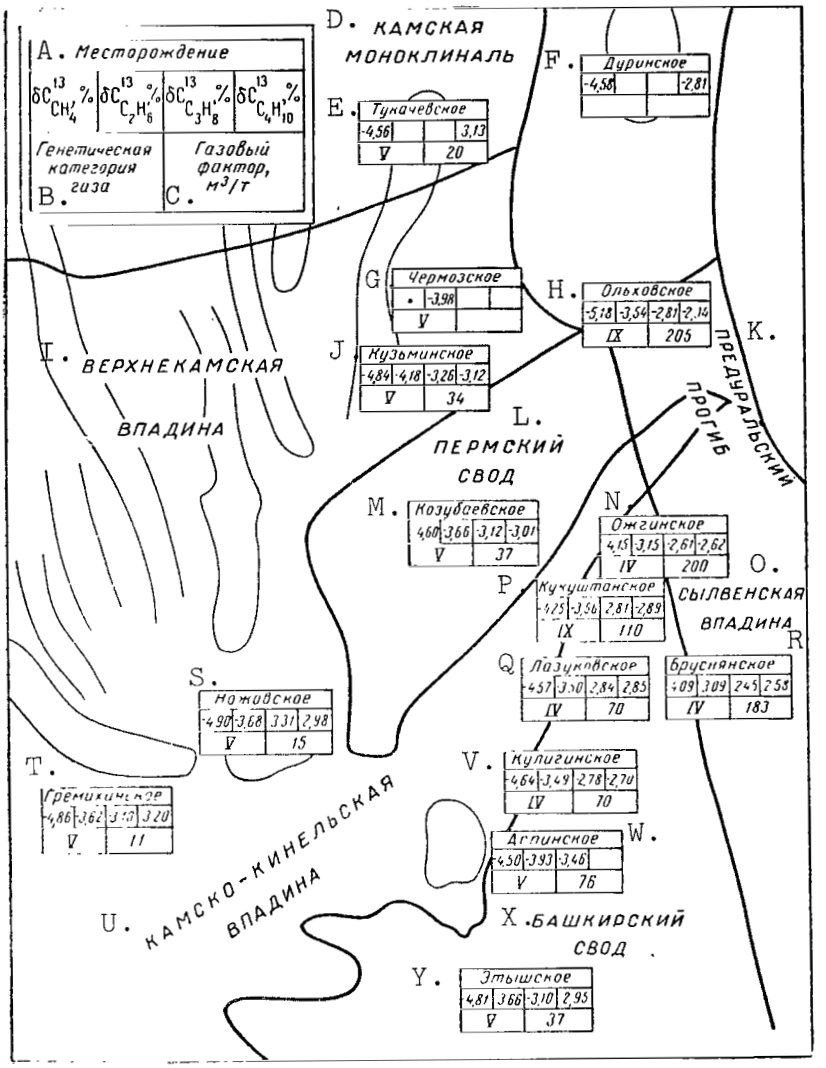

Fig. 95. Distinguishing genetical types of gases of the Yasnopolyanskiy productive complex in the Permian Ural Area through the integrated interpretation of data based on the proposed scheme of genetical identification of gases (see Fig. 94)

KEY: A. Deposit
B. Genetical category of gas
C. Gas factor, m^3/t
D. Kamskaya Monocline
E. Tukachevskoye
F. Durinskoye
G. Chermozskoye
H. Ol'khovskoye
I. Verkhnekamskaya Depression

/Key continued on following page/

/Continuation of key to Fig. 95 on preceding page./

J. Kuz'minskoye
K. Cis-Ural Trough
L. Permian Arch
M. Kozubayevskoye
N. Ozhginskoye
O. Sylvenskaya Depression
P. Kukushtanskoye
Q. Lazukovskoye
R. Brusnyanskoye
S. Nozhovskoye
T. Gremikhinskoye
U. Kamsko-Kinel'skaya Depression
V. Kuliginskoye
W. Aspinskoye
X. Bashkirskiy Arch
Y. Etyshskoye

Let us turn to the isotopic composition of carbon in the higher homologs of methane. Ethane is enriched in the light isotope ($\delta C^{13} = -3{,}54$ percent). As the value delimiting isotopically heavy and isotopically light ethane we can take $\delta C^{13} = -3{,}30$ percent. Propane is enriched in the heavy isotope ($\delta C^{13} = 2{,}81$ percent). Let us take the value $\delta C^{13} = -3{,}00$ percent as the delimiting value for propane. Thus, the distribution of isotopes in these hydrocarbons corresponds to the formula $C_2^{12}C_3^{13}$ characterizing category IX gas.

Not far from the Ol'khovskoye Deposit (within the Vasil'yevskiy Swell adjoining the zone of the Cis-Ural Trough) is the Kuz'minskoye Deposit, whose Yasnopolyanskaya pool contains, just as in the Ol'khovskoye Deposit, relatively isotopically light methane ($\delta C^{13} = -4{,}84$ percent). The ethane present in Kuz'minskoye Deposit gas is characterized by $\delta C^{13} = -4{,}18$ percent, propane -- by $\delta C^{13} = -3.26$ percent, and butane -- by $\delta C^{13} = -3{,}12$ percent. Thus, all the hydrocarbons are isotopically light. The distribution of isotopes in the hydrocarbons corresponds to the formula $C_2^{12}C_2^{13}$, characterizing category V gas. In the by-product gas of the Brusnyanskoye Deposit, methane is isotopically heavy ($\delta C^{13} = -4{,}09$ percent). In accordance with Fig. 94 it can be placed in categories V, IV, and VIII. Ethane ($\delta C^{13} = -3{,}09$ percent), propane ($\delta C^{13} = -2{,}45$ percent), and butane ($\delta C^{13} = -2{,}58$ percent) are clearly enriched in the heavy carbon isotope, which permits characterizing the distribution of carbon isotopes in individual hydrocarbons of this type with the formula $C_2^{13}C_3^{13}$ and, therefore, of placing in the genetical category IV.

By similarly interpreting data on the composition of gases from the deposits shown in Fig. 95, we can place these gases in particular genetical categories under the classification based on the scheme in Fig. 94. For Yasnopolyanskiye gases of most of the deposits in the Permian Ural Area located west of the Cis-Ural Trough, in spite of the considerable range of the variation in the isotopic composition of the gaseous hydrocarbons, the same genetical category V is characteristic. Within the /332
Cis-Ural Trough, at least the regions of it that were investigated -- the Sylvenskaya Depression and the Kos'vinsko-Chusovskaya Saddle, and also in the northeast slope of the Bashkirskiy swell directly adjoining the Cis-Ural Trough, the gases belong to categories IV and IX.

Gases of category V, with an isotopic composition of methane exhibiting δC^{13} from -4.5 to -4.9 percent, were formed at relatively early stages of the metamorphism of the organic matter enriched in lipid material. Generation of the hydrocarbons occurred in relatively mild conditions. Gases which are in category IV by isotopic composition were obtained at later stages of the metamorphism of organic matter (corresponding to coals of grades G and Zh) and in more severe temperature condition. Finally, gases of category IX are gases formed from the transformation of petroleum hydrocarbons, for example, in the thermal metamorphism of an oil pool.

Thus, gases in categories IV and IX distributed within the Cis-Ural Trough in the zone adjoining it are genetically combined with those that were formed in severe temperature conditions and in this they differ from those gases formed in mild conditions (category V) found within the platform region of the province.

If we turn to the Recent conditions of bedding of the corresponding pools, bearing in mind the burial depth of deposits and the temperature conditions in the strata, we can see that these conditions on the average were the same for pools whose gas is classified in several genetical categories. Thus, the oil pool in the Yasnopolyanskiye strata of the Ol'khovskoye Deposits is at a depth of 1840 m, in the Kukushtanskoye Deposit -- 1700 m (gases of category IX), Ozhginskoye -- 1620 m, Kulinginskoye -- -- 1610 m, and Brusnyanskoye -- 1610 m (gases of category IV). The pools in which gases relating to category V were found are approximately at the same depths, for example, the Tukachevskoye Deposits -- 1720 m, Kuz'minskoye -- 1730 m, Chermozskoye -- 1810 m, Kozubayevskoye -- 1580 m, Aspinskoye -- 1520 m, and so on. Therefore, the genetical differentiation of gases within this province is caused by the migratory origin, at least of gases in several genetical categories.

Obviously, category V gases formed in relatively mild conditions (to which the Recent conditions of their bedding in fact correspond) are, so to speak, autochthonous, possibly, syngenetic to the crudes in which they are present. Probably, most of them became dispersed during geologic time. As for gases in categories IV and IX formed in severe temperature conditions, it is logical to assume that they migrated from deeper-buried strata of the Cis-Ural Trough where these conditions existed.

Noteworthy is the fact that for the crudes whose by-product /333
gases are in categories IV and IX, very high values of the gas factors are characteristic (see Fig. 96). Taken together with the foregoing, this enables us to represent the following pattern of the formation of gases areally. Obviously, free gas formed together with petroleum hydrocarbons during the period in which the oil-gas presence was formed in the Permian Ural Area subsequently was nearly entirely lost. (Recall that in Chapter Four we concluded that the formation of oil pools in the Permian Ural Area was associated with seismic activity accompanying the Hercynian tectogenesis.) This Late Paleozoic gas was preserved only in the dissolved state in petroleum, causing the small values of the gas factor characteristic of crude oils in the petroleum part of the province (10-30 m^3/ton). The placement of the gas in genetical category V indicates that the formation of oil and gas occurred in relatively mild conditions from organic matter of the sapropelic type.

In the Cis-Ural Trough, gas accumulated under the thick strata of the Permian salt deposits in a later time, already after the consolidation of the Earth's crust in this section. It could have been formed here either from the organic matter present at this time and in these conditions at a stage of more profound metamorphism (category IV gas), as well as due to the metamorphism of crudes that were at considerable depths (category IX gas). As a result of the migration of gases into oil deposits located within the trough and adjoining provinces, the genetical types in the crudes of the corresponding deposits underwent a replacement. Simultaneously, due to the incursion of gas of younger generation there was a considerable increase in the gas factor of the crudes in the deposits found in the eastern part of the province, which also led to some variation in the composition of crudes, chiefly a reduction in their specific gravity, viscosity, loss of some of the asphalt-tarry constituents incapable of retained in the petroleum strongly enriched in light methane hydrocarbons and, as a consequence, a decrease in the sulfur content, loss of porphyrins, that is, precisely to the qualitative changes of the crudes in the Permian Ural Area that were noted by N. Ya. P'yankov and other investigators.

Chapter Four examined problems of the formation of oil pools and the migration of petroleum within the Permian Ural Area. Here a spatial differentiation of Yasnopolyanskiye crudes into crudes relating to deposits in the northwest (isotopically light) and southeast (isotopically heavy) fields was found. It was suggested that the oil pools in the southwest field formed through the migration of petroleum in a southeast to northwest direction from buried deposits of the Yurezano-Sylvenskaya Depression and the eastern slope of the Bashkirskiy swell, all /334
the way to the southeastern margin of the Kamsko-Kinel'skaya Depression, blocking the path of the migratory flow within the Lower Carboniferous strata. The traps within the northwest field embracing deposits of the Kamsko-Kinel'skaya Depression as such and part of its southeast margin, the Permskiy swell, and the Vyatsko-Kamskaya Depression were filled in another manner and from another source, namely as a result of the variously directed local migration from petroleum-parent strata developed in the actual zone of petroleum and gas accumulation.

The distribution of gases by isotopic composition (by genetical categories) as we have seen is altogether distinct from the distribution of the crudes. Most of the gases in the platform part of the Cis-Ural Trough are in category V regardless of the genetical origin of the corresponding crudes. At the same time, crude oil from the Ol'khovskoye Deposit located in the trough containing gas that is highly specific in its properties (category IX) does not differ in isotopic composition from the crudes in other Yasnopolyanskiye pools in the northwest field. Exactly the same is true of the Ozhginskoye, Kuliginskoye, and other deposits, whose gas is assigned to genetical category IV, and whose crudes are placed by isotopic composition among the typical deposits of the southeast field.

Thus, gases of the Permian Ural Area, as shown by the results of isotopic analyses have their own geological history distinct from that of the crudes. The establishment of a gas presence occurred through the accumulation at an ancient (Late Paleozoic) gas field -- significantly depleting itself through dissipative processes -- of gases from a younger generation formed in buried strata of the Cis-Ural Trough. In a west-to-east direction one can observe a shift in the genetical types of gas (see Fig. 95), as well as an increase in the gas saturation of crudes, that is, the rising influence of the imposed gas flow.

Based on this pattern of the formation of Permian Ural Area pools, we can make several predictions. The fact of gases migrating from the Cis-Ural Trough established by the isotopic composition of carbon makes promising the expansion of geological-prospecting work in this province.

It is essential that the gases arriving from buried strata of the Cis-Ural Trough relate not to VI or VII categories (see Fig. 94) of gases, unpromising with respect to petroleum hydrocarbons. Category IV gases are gases formed along with crudes, while category IX gases were formed from crudes. Therefore it can be expected that in the strata of the Cis-Ural Trough that are sources of migrating gases there are also oil pools. Based on the distribution of carbon isotopes in gases, oil and gas promising strata are those in the Sylvenskaya Depression and the buried strata of the Kos'vinsko-Chusovskaya saddle.

CHAPTER SEVEN /335

ENDOGENIC CARBON

Primordial Carbon of Mantle

A characteristic feature of the distribution of carbon isotopes in endogenic minerals is the presence of two groups of carbonaceous compounds differing in isotopic composition. The first consists of minerals genetically associated with the concentrated form of mantle carbon and its degassing products (these are carbon dioxide, methane, diamonds, carbonatites, certain graphites, and hydrothermal carbonates); the latter is made up of minerals genetically associated with the diffuse form of mantle carbon. The former contain isotopically heavy carbon (δC^{13}_{av} = = 0.7 percent), and the latter -- isotopically light carbon (δC^{13}_{av} = 2.5 percent).

In 1966, at the First All-Union Symposium on Stable Isotopes the author advanced a hypothesis on the singular role of material of the carbonaceous chondrite type in forming the Earth's mantle /35/. The basis for this hypothesis was data on the distribution of carbon isotopes in endogenic minerals, and also calculations of the mean isotopic composition of carbon in the Earth's crust. The latter, as was shown, is characterized by a value δC^{13} from -0.5 to -0.8 percent /26/. At the same time, ordinary stony meteorites (ordinary chondrites), which are assumed to be the principal prototype of mantle material, have an essentially different isotopic composition of carbon ($\delta C^{13}_{av} \cong -2.2$ percent). The question of precisely what type of material (corresponding to what meteoritic type) served as the primordial material at /336 the time of the Earth's formation is of fundamental significance, since the chemical composition of the primordial mantle ultimately determined the geologic and chemical history of the Earth.

Carbonaceous chondrites contain up to 2-4 percent carbon (type I), usual chondrites -- 0.04 percent, and iron meteorites -- 0.08 percent /15/. Carbon in carbonaceous chondrites for the

most part is present as high-carbon aromatic polymers. A number of individual organic compounds have been detected and isolated: amino acids, phenols, and hydrocarbons, including isoprenoids [157, 164, 190]. Measurements of the isotopic composition of carbon made by A. P. Vinogradov et al. [61], and by foreign investigators [119, 121, 132, 181, and so on] showed that the isotopic composition of carbon in individual components varies over a very broad range of δC^{13} values -- from +6.0 percent characterizing carbonates, to (-1.5) - (-3.0 percent) characterizing extractible organic compounds of carbon. The isotopic composition of the carbonaceous mass of meteorites overall corresponds to a δC^{13} value of about -0.7 percent [119, 121] (for carbonaceous chondrites of types I and II). This is the value of the mean isotopic composition of the earth's crust [26].

In addition to the high carbon concentrations, carbonaceous chondrites contain much water, while there is very little of it in ordinary chondrites. It is possible that by virtue of the features of the geologic scene, including the presence of oceans as well as the carbon-water mode of life, that the earth is indebted by the fact that its mantle or some part of it during the formation of the earth inherited the material of the carbonacous chondrite type, which did not happen -- for example -- during the formation of the moon or Mars. Not only carbon, but also other elements of the earth and carbonaceous chondrites disclose a similarity of isotopic composition. This involves above all the elements that entered the earth's crust during degassing of the mantle. Thus, the isotopic composition of hydrogen D/H in ocean water is $154 \cdot 10^{-6}$, that of carbonaceous chondrites -- $159 \cdot 10^{-6}$, while in ordinary stony meteorites -- $135 \cdot 10^{-6}$; the isotopic composition of neon (Ne^{20}/Ne^{21}) for the earth's crust, carbonaceous chondrites, and ordinary chondrites is characterized by the values -- respectively -- of 0.002, 0.004, and 1; the values of Ar^{36}/Ar^{38} in the corresponding materials are 5.35, 5.1, and 2.0, while the values for Xe^{129}/Xe^{131} are 1.24, 1.28, and 1.79.

A more detailed discussion of the possible genetical commonality of the material of the earth and the material of the carbonaceous type is given in studies by the author [26, 29]. At the present time, this problem will be touched on to the extent that the nature of the primordial material of the mantle determines the isotopic composition of the plutonic juvenile carbon and therefore, the starting-point from which one must estimate the fractionation of carbon isotopes in endogenic processes.

Fig. 96 presents data on the isotopic composition of various forms of carbon from igneous and metamorphic rocks. It should be noted that the isotopic composition of gases and bitumens in igneous rocks has been studied most closely by Soviet investigators. [337]

Work by foreign researchers includes data on the isotopic composition of a number of endogenic forms of carbon: diamonds [68, 234], carbonatites [160, 226], travertines [159], hydrothermal carbonates [153, 141, 142], graphites [187, 188, 154, 209, 165], gases of thermal regions [68, 170, 147, 162], and bitumens [169, 183]. Most of these data are presented in summarizing studies by the author [26, 29].

Shown in Fig. 97 is the general scheme of the fractionation of carbon isotopes in the endogenic process. Mantle carbon inherited from carbonaceous chondrites, being present in a concentrated form in an environment rich in hydrogen as well as in iron oxides, proved to be most reactive and was introduced into the earth's crust in the form of the gaseous compounds CO, CH_4, and CO_2. Carbon belonging to this line (the first line of the evolution of mantle carbon) [26] has an isotopic composition analogous to that for total carbon in carbonaceous chondrites (δC^{13} = -0.7 percent). It is precisely along this path that most of its carbon entered the earth's crust from the mantle (about 95 percent, according to A. P. Vinogradov) [14], which accounts for the fact that crustal carbon is relatively heavy carbon.

Minerals genetically associated with endogenic carbon dioxide and formed at elevated temperatures exhibit an isotopic composition, as a rule, that is close to -0.7 percent. The isotopic composition of most diamonds from various parts of the world is about -0.6 percent. In Fig. 96 are shown the results -- obtained by us and V. V. Koval'skiy -- of an isotopic analysis of colored varieties of Yakutsk diamonds representing an exception from the general rule (their enrichment in C^{12} reaches values of δC^{13} = = - 2.2 percent, and in one sample δC^{13} = -3.2 percent). The reasons that may have accounted for the appearance of diamonds having an uncommon isotopic composition were examined earlier [33]. As a whole, diamonds pertaining to the first line of evolution of mantle carbon have δC^{13} from -0.3 to -0.8 percent. Carbonatites fall into the same range. Carbonatites were formed through the action of carbon dioxide-rich postmagmatic solutions on silicate minerals. Together with Yu. A. Boagdasarov and V. S. Prokhorov [2], we investigated the isotopic composition of ankeritic (ferruginous) carbonatites (Eastern Siberia). It was found that they are depleted in C^{12} (δC^{13} from -0.92 to -0.45 percent), in contrast to most earlier-studied specimens (Fig. 96). This phenomenon is associated with features of isotopic exchange in systems containing iron ions. Overall, the isotopic composition of carbonatites is -0.6 to -0.7 percent, characteristic of minerals in the first line of the evolution of mantle carbon.

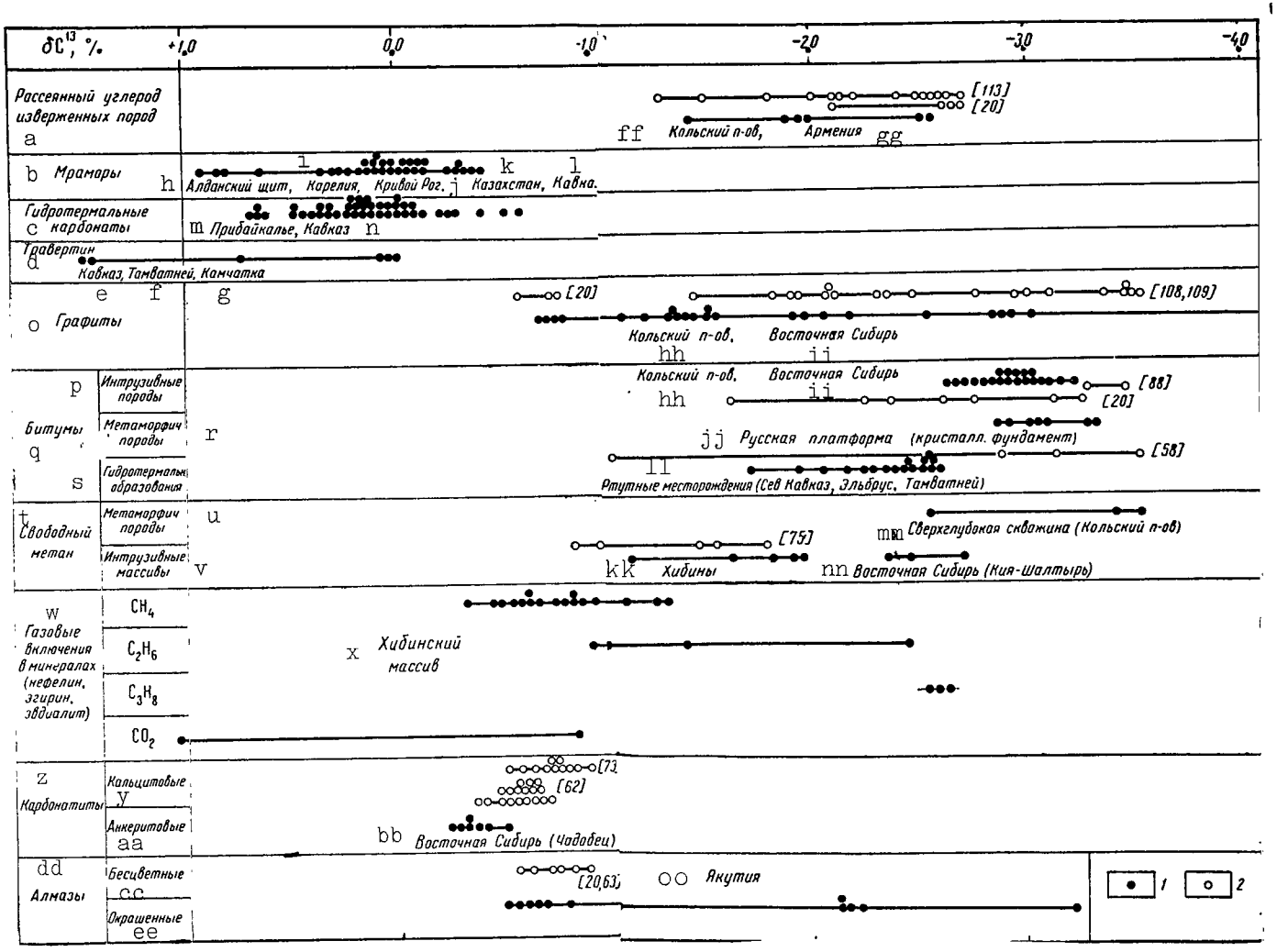

Fig. 96. Isotopic composition of endogenic forms of carbon analyzed in the USSR

1. data of author (Tables 78-84) 2. data of other investigators

KEY: a. Diffuse carbon of igneous rocks
b. Marbles
c. Hydrothermal carbonates
d. Travertine
e. Caucasus
f. Tamvatney

/KEY continued on next page/

/KEY to Fig. 96, concluded/
g. Kamchatka
h. Aldanskiy Shield
i. Karelia
j. Krivoy Rog
k. Kazakhstan
l. Kavka
m. Baykalia
n. Caucasus
o. Graphites
p. Intrusive rocks
q. Bitumens
r. Metamorphic rocks
s. Hydrothermal formations
t. Free methane
u. Metamorphic rocks
v. Intrusive masses
w. Gas inclusions in minerals (nepheline, aegirite, eudialyte)
x. Khibin massif
y. Calcitic
z. Carbonatites
aa. Ankeritic
bb. Easterr Siberia (Chadobets)
cc. Colorless
dd. Diamonds
ee. Colored
ff. Kola Peninsula
gg. Armenia
hh. Kola Peninsula
ii. Eastern Siberia
jj. Russian Platform (crystalline foundation)
kk. Khibiny Range
ll. Mercurcy deposits (Northern Caucasus, El'brus, Tamvatney)
mm. Extra-deep bore hole (Kola Peninsula)
nn. Eastern Siberia (Kiya-Shaltyr')
oo. Yakutia

Gaseous compounds of carbon formed in the mantle at high temperatures directly inherited the isotopic composition

Gaseous compounds of carbon formed in the mantle in high temperature conditions directly inherited the isotopic composition of the primordial carbon. Volcanic carbon dioxide is characterized by the value $\delta C^{13} = -0.8$ percent, corresponding to the isotopic composition of carbonaceous chondritic matter. Endogenic methane is also among the mobile compounds of carbon transported from the mantle along with carbon dioxide. However, the determination of the isotopic composition of methane in volcanic gases and thermal springs showed that it is enriched in C^{12} (δC^{13} from -2.1 to -2.9 percent) [68, 147, 162, 170]. This effect is secondary. It is caused by the isotopic exchange in the system CO_2 - CH_4, which for the sampling conditions of the volcanic gases analyzed (300-500° C) is characterized by an appreciable value of the partition coefficient ($\alpha = 1.016$ at 400°C). The amount of CO_2, as shown by analyzes of volcanic and thermal gases, exceeds the amount of CH_4 by 10 to 100 times, therefore as a result of the separation of isotopes in the system CO_2 - CH_4 virtually only the isotopic composition of CH_4 will change (by only the amount determined by the partition coefficient), and the isotopic composition of CO_2 will remain practically the same. /341

To determine the primordial isotopic composition of endogenic methane, it must be sought for in the conditions where it is not in contact with carbon dioxide. Therefore, with I. A. Petersil'ye we analyzed gaseous inclusions in minerals of igneous rocks having predominantly methane composition, in which heavy methane with an isotopic composition characterized by δC^{13} from -0.28 to -1.3 percent was actually established [47].

The second line of evolution of carbon ascends to the diffuse material of the mantle and meteorites. If the concentrated carbon in a mantle of the carbonaceous chondrite type readily forms the gaseous compounds transported from the mantle, carbon in the diffuse form, as was shown experimentally [26], is stable and constitutes the residual phase of carbon that enters the earth's crust only as part of an intrusion. The diffuse carbon in the mantle corresponds to the diffuse form of carbon in stony meteorites, which is characterized by a relative enrichment in the light isotope ($\delta C^{13} = -2.2$ percent). In igneous rocks, including ultrabasic and basic rocks, the diffuse carbon is presently approximately in the same concentrations (according to A. P. Vinogradov -0.04 percent) as in ordinary stony meteorites.

The isotopic composition of carbon in a series of dunites and basalts determined by V. S. Prokhorov varied from -2.3 to

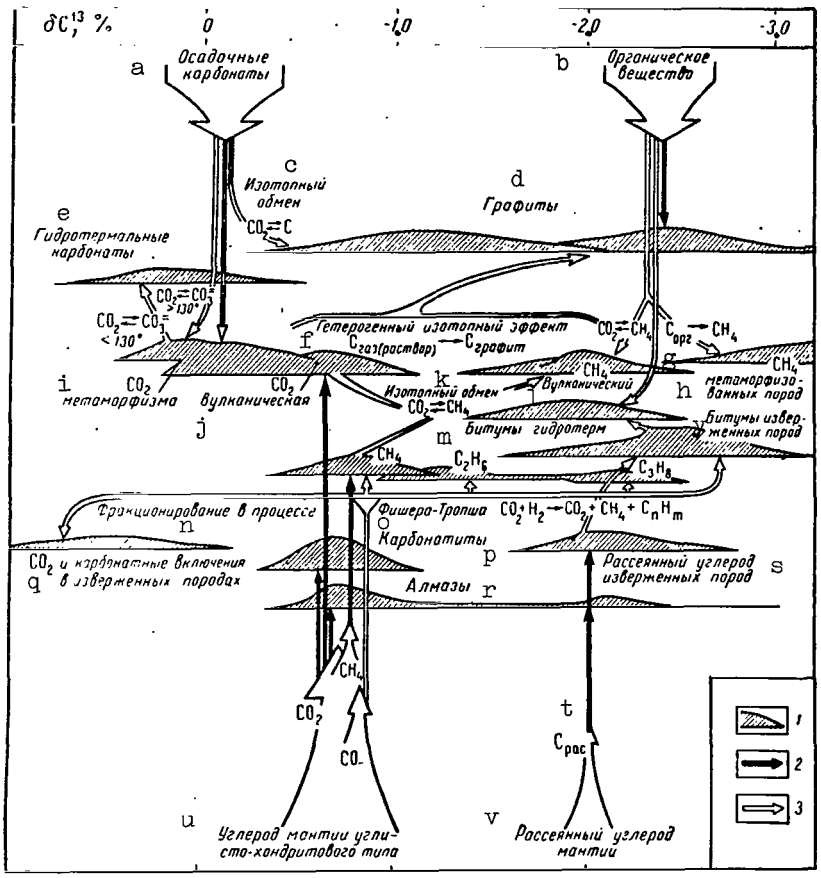

Fig. 97. Scheme of formation of isotopic composition of endogenic forms of carbon

1. distribution of δC^{13} values characterizing given compound in endogenic conditions
2. processes culminating with the inheritance of the isotopic composition of the initial compound
3. processes accompanied by isotope fractionation (type of separation reaction is indicated next to arrow)

KEY: a. Sedimentary carbonates
b. Organic matter
c. Isotopic exchange
d. Graphites
e. Hydrothermal carbonates
f. Heterogenic isotope effect $C_{gas(solution)} \rightarrow C_{graphite}$
g. C_{org} /KEY concluded on next page/

/KEY to Fig. 97 concluded/

h. CH_4 of metamorphosed rocks
i. CO_2 of metamorphism
j. Volcanic CO_2
k. Isotopic exchange
l. Volcanic CH_4
m. Bitumens of thermal springs
n. Fractionation in
o. Fischer-Tropsch process
p. Carbonatites
q. CO_2 and carbonate inclusions in igneous rocks
r. Diamonds
s. Diffuse carbon in igneous rocks
t. C_{dif}
u. Carbon in mantle of carbonaceous chondrite type
v. Diffuse carbon in mantle

-2.6 percent, which fits within the range of variation of δC^{13} established earlier /14, 113, 68/ for this form of carbon. The mean value of δC^{13} of diffuse carbon in igneous rocks is -2.27 percent.

Fractionation of Carbon Isotopes in High-Temperature Processes /342

Separation of Isotopes in Equilibrium Systems

The participation of mantle carbon in the endogenic process is one of the characteristic features of the geochemistry of endogenic carbon. A second feature is the absence of the biological factor. Therefore, there are no biogenic intramolecular isotope effects, which -- as we have seen -- play such a significant role in the geochemistry of isotopes of exogenic forms of carbon. On the other hand, thermodynamic isotope effects of the second order (see Chapter Two) take on large importance, since high temperatures open up the possibility of a direct isotopic exchange between various carbon compounds. Whereas at temperatures characteristic of the normal profile of sedimentary rocks (to 100° C) we can neglect the possibility of secondary isotopic exchange in the system CO_2 - CH_4, already in mesothermal springs, volcanic gases, and intrusions the isotopic exchange in this system quite rapidly attains equilibrium. Isotopic exchange between the constituents of hydrocarbon gas $CH_4—C_2H_6—C_3H_8—C_4H_{10}$, as shown in Chapter Four, virtually does not take place at temperatures of

50-100° C, but at temperatures above 300° C equilibrium can be established in a geologically, very short time interval.

At the present time, β-factors have been calculated for all the principal carbon compounds participating in high-temperature processes. Table 76 lists the values of the isotopic shifts characterizing the separation of carbon isotopes in the systems most typical of endogenic conditions. The isotopic shift at a given temperature determines the C^{13} enrichment (in percent) of the first term of the system compared with the second, for example $\Delta(CO_2 - CH_4) = \delta C^{13}_{CO_2} - \delta C^{13}_{CH_4} = \left(\frac{\beta CO_2}{\beta CH_4}\right) - 1 \cdot 10^2 \approx 10^2 \ln \alpha$.

We must point to the main features of the attainment of equilibrium of isotopic exchange in systems of polyatomic compounds caused by the presence of nonequivalent atoms.

When there is isotopic exchange between compounds containing one exchangeable atom or equivalent atoms, the distribution coefficient during the attainment of equilibrium varies monotonely from $\Delta(t_0) = 1$ (we have in mind that the initial composition of the reacting compounds was the same) to $\Delta(t_\infty) = \alpha$. In polyatomic compounds containing nonequivalent atoms of the exchangeable element, the nature of the change in the distribution coefficient during the attainment of equilibrium can be different. Here the quantity $\Delta(t)$ depends on the rates of exchange of atoms in the corresponding positions. For example, for acetic aldehyde /343 at 300° K $\beta_\Sigma = 1.151$, $\beta_I = 1.160$, and $\beta_{II} = 1.141$, where the subscripts I and II stand for the β-factors for the carbon in the aldehyde group and the radical, respectively. For propynal at 300° K, $\beta_\Sigma = 1.154$, $\beta_I = 1.196$, and $\beta_{II} = \beta_{III} = 1.132$, the subscript I refers to the aldehyde group, and II and III -- to the radical atoms.

Obviously, at the state of equilibrium

$$\alpha_{300^\circ K} = \frac{\beta_{\Sigma_{C_2HCHO}}}{\beta_{\Sigma_{CH_3CHO}}} = 1.003$$

But if the rate of carbon exchange in the aldehyde groups of these compounds is greater than the exchange rate for the carbon in the radicals, the instantaneous coefficient of distribution will be determined mainly by the ratio of the β_I-factors characterizing the substitution of carbon in the aldehyde group, that is,

$$\Delta(t) = \frac{\beta_{I_{C_2HCHO}}}{\beta_{I_{CH_3CHO}}}$$

This quantity is 1.039 at 300°K, that is, it is much larger than the equilibrium value.

Similar inversional principles are possible also in the manifestations of the kinetic isotope effect, which is usually considered as a consequence of the predominant rupture of $C^{12}-C^{12}$ bonds compared with $C^{12}-C^{13}$ bonds. Let us examine, for example, the reaction $CO + 3H_2 \rightarrow CH_4 + H_2O$. The kinetic isotope effect of this reaction is determined by the dissimilar rate of hydrogenation of $C^{12}O$ and $C^{13}O$, which must lead to the formation of isotopically light methane. But one cannot state definitely that the rupture of C-O bonds is the limiting stage of this reaction.

The reaction can proceed, for example, by the following mechanism:

$$1)\ C{=}O + H{-}H \rightleftarrows H{-}\underset{\displaystyle H}{\overset{\displaystyle |}{C}}{=}O.$$

If equilibrium is attained at this stage, the isotope effect is determined by the thermodynamic isotope effect in the system CO - HCOH. In this system, HCOH is enriched in the C^{13} isotope (see Table 26):

$$2)\ H{-}\underset{\displaystyle H}{\overset{\displaystyle |}{C}}{=}O + H{-}H \rightleftarrows H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{C}}}{-}OH.$$

The isotopic composition of CH_3OH depends on the relative rates of the first and second reactions. If then at this stage equilibrium is reached, the resultant isotope effect is determined by the thermodynamic isotope effect in the system CO - CH_3OH. /344

In this system, as follows from Table 26 of the thermodynamic isotope factors, alcohol is enriched in C^{13} relative to CO, but to a lesser extent than aldehyde:

$$3)\ H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{C}}}{-}OH + H{-}H \longrightarrow H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{C}}}{-}H + H_2O.$$

At this stage the C-O bond is broken. Owing to the predominant rupture of $C^{12}-O$ bonds, the methane formed must be enriched in C^{12}. But if the alcohol is in equilibrium with the CO and is enriched in C^{13}, the methane can be isotopically heavier than the

initial compound, counter to general considerations on the predominant reactivity of $C^{12}O$ molecules.

The possibility of these anomalies must be borne in mind, when examining the high-temperature processes of isotope fractionation, where secondary reactions of isotope exchange (thermodynamic isotope effects of the second order) are advanced to the fore. In low-temperature conditions these reactions are greatly inhibited and there the main role is played by the isotopic shifts caused by the intramolecular isotopic nonuniformity of biogenic compounds. Secondary effects in most cases are such that they can be neglected.

Fischer-Tropsch Process

The Fischer-Tropsch process is usually regarded as the most probable chemical model of the abiogenic synthesis of organic compounds in nature. This involves both the possible formation of organic compounds in space conditions, for example, those prevailing in carbonaceous chondrites, as well as in hydrocarbons and bitumens encountered in igneous rocks. As we know, the view is also held that greater significance lies in the inorganic synthesis of hydrocarbons, associating with this process the genesis of petroleum and natural gas.

The fractionation of carbon isotopes in the Fischer-Tropsch process was investigated by M. Lancet and E. Anders [185]. The experiment was conducted at 400° K, a pressure of 1 kg/cm^2, at equimolar volumes of CO and H_2, and in the presence of a cobalt catalyst.

During the reaction both oxidized and reduced products are formed: /345

$$n\mathrm{CO} + (2n+1)\,\mathrm{H_2} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O};$$

$$2n\mathrm{CO} + (n+1)\,\mathrm{H_2} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{CO_2}.$$

Most of the CO oxygen passes into the H_2O, but some enters the carbon dioxide, whose content in the reaction products is several tenths of a percent. Among the reduced products there is a predominance of methane (69-88 percent by the end of the reaction). The content of hydrocarbons, volatile at 400° K (C_{2+}), reaches 3 percent, approximately, by the end of the experiment. Some of the polymerized organic compounds (about 1.5 percent) not sublimated at 400° K remains on the catalyst (coke). The results of the isotopic analysis of carbon in the reaction products in the experiments of M. Lancet and E. Anders are shown in Fig. 98.

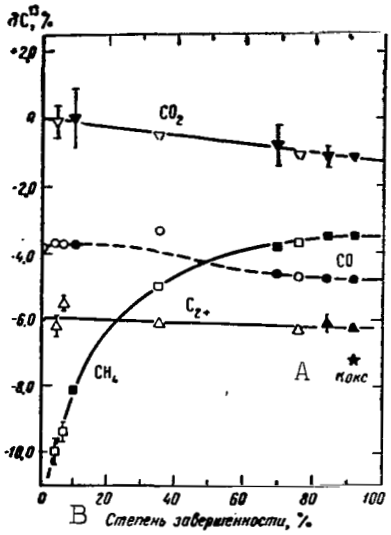

Fig. 98. Fractionation of carbon isotopes at different stages of Fischer-Tropsch reaction (after M. Lancet and E. Anders) [185]. Open and black symbols correspond to two parallel experiments.
KEY: A. Coke
B. Degree of completion, percent

The carbon dioxide formed in the Fischer-Tropsch process is approximately 3.5 percent enriched in C^{13} relative to the carbon in the initial CO. And this difference remains more or less constant during the reaction. The carbon in the C_{2+} fraction, in contrast, is about 1.9 percent enriched in the light isotope. The high-molecular product remaining on the catalyst is characterized by a still higher enrichment in the light isotope -- by 3.3 percent relative to the CO carbon. The carbon in methane formed at the beginning of the reaction is most enriched in the light isotope. At this point, the difference between the isotopic composition of the carbon in CO_2 and CH_4 reaches 10 percent, while for the carbon in CO and CH_4 shows a 6 percent difference. As the reaction progresses, methane is rapidly depleted in the light isotope. Since methane is the predominant reaction product, its isotopic composition begins to approach that of the initial CO. In addition, obviously the isotopic exchange in the system CO - CH_4 plays a role, owing to which the methane in the last stages of the process becomes heavier than the CO, as follows from the equilibrium constants of isotopic exchange for this system (see, for example, Table 76). Here, however, we must bear in mind that the rate of isotopic exchange between CO and CH_4, to all appearances, is quite low. M. B. Neyman et al analyzed the isotopic exchange in this system, using carbon monoxide labelled with the radioactive isotope C^{14}. The mixture $C^{14}O + CH_4$ was kept at 700-800° K for 4-10 hr. Then only 0.003-0.006 percent of the carbon monoxide activity was found in the methane [85].

Epitaxial Growth of Diamond and Graphite

An isotope effect of a new type was found in the epitaxial growth of diamond and graphite [31, 93].

TABLE 76. ISOTOPIC SHIFTS ΔC^{13} (PERCENT) $\approx 10^2 \ln \alpha$ CHARACTERIZING SEPARATION OF CARBON ISOTOPES IN ISOTOPE-EXCHANGE SYSTEMS AT DIFFERENT TEMPERATURES /346

Isotope-exchange system	Temperature, °K				
	300	400	600	800	1000
$CO_2 - CH_4$	6.79	4.38	2.30	1.40	0.96
CO_2 — Graphite	1.46	1.50	1.27	0.98	0.74
$CO_2 - CO$	8.30	5.39	2.80	1.79	1.19
$CH_4 - C_2H_6$	−1.62	−0.89	−0.32	−0.14	−0.06
$CH_4 - C_3H_8$					
$CH_4 - C_6H_6$ (benzene)	−3.43	−1.95	−0.71	−0.32	−0.10
$CH_4 - C_6H_{12}$ (cyclohexane)	−3.66	−2.02	−0.77	−0.34	−0.18
CH_4 — C graphite	−5.33	−2.88	−1.03	−0.42	−0.22
$CH_4 - CO$	1.51	1.01	0.50	0.39	0.23

Diamond and graphite were synthesized from methane at temperatures of 1000-1050° C and a methane pressure 0.2-0.5 mm Hg, by a method described in a paper by B. V. Deryagin and D. V. Fedoseyev /54/. Deposition was carried out on a diamond substrate. Diamond growth was accompanied by the synchronous formation of nondiamond carbon (graphite or amorphous carbon), which was periodically removed. Diamond growth was achieved through the frequent repetition of the cycles of synthesis and cleaning. If no cleaning was done, diamond growth stopped and only graphitic carbon grew.

Isotopic analysis revealed the enrichment of the newly formed diamond in the heavy carbon isotope. For the isotopic composition of the starting methane characterized by $\delta C^{13} = -4.62$ percent, the synthesized diamond had δC^{13} values in the series of experiments from -2.01 to -2.65 percent, that is, on the average the C^{13} enrichment was 2.3 percent (Fig. 99).

The measured isotopic composition of graphite formed together with diamond was -6.75 percent, which means that the graphitic carbon, in contrast, was enriched in the light isotope. Graphite was /347 synthesized also independently of diamond, with carbon black used as the substrate. The synthesized graphite had $\delta C^{13} = -6.58$ percent, and therefore, in this case as well the graphite was enriched in C^{12} by about 2.0 percent. The high degree of fractionation was amazing at temperatures of synthesis this high, as well as the different sign of the isotope effect for graphite and diamond. We recall that the β-factors of graphite and diamond, as found by H. Urey /229/ and Y. Bottinga /123/ and as follows from the calculation of the isotopic bond numbers (see Table 27) are approximately the same. Also, the partition coefficient in the system CH_4 - $C_{diamond}$ at 1050° C at which the synthesis was carried out became negligibly small (even at 325° C it was 1.006 and

continued to decrease with increase in temperature, while the experimentally observed partition coefficient was about 1.025). Moreover, for synthesis from methane the thermodynamic isotope effects for diamond and graphite must have the same sign.

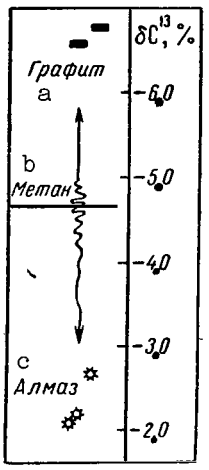

Fig. 99. Range of fractionation of carbon isotopes in the synthesis of diamond and graphite from methane
KEY: a. Graphite
b. Methane
c. Diamond

The paper [31] presents a more detailed examination of a possible mechanism of the observed isotopic fractionation, which in our view is associated with the competition of rates and isotope effects of van der Waals and activation adsorption phenomena. From a discussion of the model we proposed [31], the conclusion is drawn that the isotope effect for diamond (enrichment in C^{13}) must increase with temperature rise. The isotope effect for graphite must have a maximum at a specific temperature and decrease with deviation of the temperature from the optimal value. The pressure rise in the general case is operative counter to the temperature increase.

The heterogeneous isotope effect of the kind described here evidently plays a marked role in the formation of the isotopic composition of hydrothermal graphites.

Oxidation of Hydrocarbons

When hydrocarbons were oxidized in a laboratory installation for the preparation of samples for mass spectrometric analysis, isotope fractionation was observed. Table 77 gives the results of an analysis of the phenomenon. The gaseous hydrocarbons were oxidized in a closed system, where the gas was circulated through a reactor filled with copper oxide. The latter served as the only oxidizer. The experiment was conducted at different temperatures.

Analysis of the isotopic composition of the CO_2 produced at different degree of process completion showed that oxidized carbon was enriched in the heavy isotope.

The δC^{13} values were calculated based on the assumption that the gas mixture consisted only of CO_2 and CH_4. Actually, CO was prominent among the oxidation products.

TABLE 77. DEPENDENCE OF ISOTOPIC COMPOSITION OF CO_2 CARBON ON ITS YIELD IN THE OXIDATION OF METHANE /348

Reactor temperature, °C	Oxidation time, min.	CO_2 yield %	δC^{13}, %	ΔC^{13}, %
600	120	100	−4,87	+0,01
700	60	100	−4,88	0,00
800	40	100	−4,88	0,00
800	30	100	−4,89	−0,01
800	20	100	−4,88	0,00
900	10	100	−4,91	−0,03
700	20	79	−4,63	+0,25
800	10	87	−4,82	+0,06
800	5	68	−4,52	+0,36
700	5	35	−3,94	+0,94
600	5	10	−3,11	+1,97
800	0,5	24	−3,92	+0,96

Experiments with heavier hydrocarbons, all the way to butane, yielded similar results. But when liquid hydrocarbons were oxidized, isotope effects of this kind were virtually absent. This fact, as well as the sign of the isotope effect -- in agreement with the sign of the thermodynamic isotope effect -- affords grounds to assume that during oxidation isotopic exchange of CO_2 carbon occurs either directly from hydrocarbons, or through the CO form.

The mechanism of isotope fractionation requires further study, but even now it can be concluded that when in nature conditions for the partial oxidation of gaseous hydrocarbons are provided at high temperatures (600-900° C), the CO_2 formed is enriched in the heavy carbon isotope.

Sublimation of Bitumens From Rocks /349

In an experiment conducted by S. V. Ikorskiy, natural bitumen was isolated from eudialyte at temperatures of 680-720° C. Heating was carried out in a Pyrex ampule with a side arm, from which the air had first been evacuated. Opening up of inclusions containing the bitumens began at 500° C; the vapors released were condensed on the cold walls of the side arm tube. In ultraviolet light the following differentiation was observable: the fractions luminescing with brown light condensed closer to the heater, next -- with yellow light, and finally, the condensate giving off a blue glow. The isotopic composition of the latter was found not possible to analyze. Measuring the isotopic composition of the first two fractions showed a marked fractionation of isotopes. The "high-boiling" bitumen fraction had $\delta C^{13} = -3{,}53$ percent, and the relatively "low-boiling" fraction (corresponding to the section with a yellow glow) had $\delta C^{13} = -2{,}88$ percent. The isotope effect observed

depends both on differences in the isotopic composition of the fractions of the starting bitumenoid, as well as on the fractionation resulting from the cracking of the bitumen, and possibly, also on the heterogeneous isotope effects. Overall, it may be concluded that the total isotope effect of the sublimation of bitumens leads to the depletion of the least volatile fractions in the heavy isotope.

Carbonaceous Material in Endogenic Conditions

Graphites

The formation of graphite through profound metamorphism of organic matter as a rule was not accompanied by isotope fractionation. In this case, the graphite can be regarded as the extreme member of the coalification series. Investigations showed that during the metamorphism of coals no marked change in the composition of carbon takes place. Accordingly, the graphites from crystalline shales are generally isotopically light, coinciding in isotopic composition with the organic matter of sedimentary rocks [29, 154, 188].

Along with the graphite enriched in the light isotope, graphite of relatively heavy isotopic composition is encountered. Graphite associated with limestones is usually depleted in the light isotope compared with the graphite in crystalline shales. It is assumed that in these cases the initial carbon of graphite was the carbon of sedimentary carbonates subjected to contact metamorphism [65, 188, 209].

Table 78 gives examples of graphites whose carbon -- as to isotopic composition -- is intermediate between the isotopically light carbon of the "organic line" graphites and the isotopically [351] heavy carbon of the "carbonate line."

The above-described experiments involving the synthesis of graphite and diamond from methane showed that heterogeneous fractionation of isotopes is present in the epitaxial growth of the solid phase. This permits bringing into consideration yet another important mechanism of the natural separation of carbon isotopes.

Graphite and noncrystalline carbon can be precipitated on practically any surface. Undoubtedly, this process is widely found in nature. Deposition of graphite, for example, from hydrothermal solutions containing low concentrations of carbon compounds in the form CO_2 and CH_4 or others is wholly analogous to the deposition of graphite from the gas phase at low pressures.

TABLE 78. ISOTOPIC COMPOSITION OF SEVERAL GRAPHITES ANALYZED

/350

Sampling Site	Characteristics of Sample	δC^{13}
Kiya-Shaltyrskiy massif of urtites (Eastern Siberia)	Graphite from altered urtite of central part of massif	-1.54
	Graphite from altered urtite near contact with intervening rocks (marblelized limestones of Kondomskaya suite)	-1.37
Khibiny Range, Mt. Kukisvumchorr, zone of ritschorrites	Carbocer from natrolitized feldspathic-nephelinic pegmatite vein	-2.56
Khibiny Range, Mt. Yukspor	Graphite forming a pseudomorphism in aegirite in aegirite-apatite-natrolite vein. Carbon content in mixture with aegirite exceeds 50 percent.	-1.52
	Graphitic veinlet of fissured zone of altered urtites	-1.40
	As above	-1.37
	Carbonaceous matter from limestones of Kondomskaya suite 1.5 km from the body of urtites	-2.07
Sakharioskiy alkaline massif of syenites and nephelinic syenites (Kola Peninsula)	Graphite in microcline of contact of plagiogranite in miaskite	-0.76
	As above	-0.74
Khibiny Range, Takhtarvumchorr ridge, central zone of pegmatite, ore body of molybdenum mine (Kola Peninsula)	Fine-grained rock with graphite (feldspar with nepheline, molybdenite, and 4-6 percent finely dispersed graphite)	-1.43
Khibiny Range, Gakmana gorge	Graphite in pegmatite	-1.37
Central Keyvy Range, Mt. Tepysh-Maton	Finely concreted kyanitic shale	-2.92
Central Keyvy range, Mt. Shuururta	Sheaflike-fibrous kyanitic shale	-4.70

/TABLE concluded on next page/

/TABLE 78 concluded/

Sampling Site	Characteristics of Sample	δC^{13}, percent
Pechenga, Lake Poroyarvi (Kola Peninsula)	Carbonaceous phyllite from vulcanogenic-sedimentary strata (Middle Proterozoic, Pechengskaya Series)	-2.94
	Fine-plicated black sulfide shale containing carbonaceous (shungitic) material: shungite -- 82.9 percent, sulfide -- 6.1 percent, and quartz -- 11 percent.	-2.89

We studied the isotopic composition of several graphites from hydrothermally altered urtites of the Kiya-Shaltyrskiy alkaline-basic massif (Kuznetskiy Alatau). According to field observations by S. V. Ikorskiy, graphite mineralization is confined to the zones of fissuring and cataclasis along which rock has been subjected to intensive hydrothermal working. Graphite forms thin seams, sometimes intersecting individual grains of altered nepheline. The isotopic composition of this graphite in different samples varies from -1.37 to -1.54 percent. Still, in all probability, the source of the carbon in hydrothermal solutions was the carbonates of the sedimentary-effusive Kondomskaya suite and was formed by marblelized limestones of the Usinskaya (CT_1) suite, and the contact with these limestones marks the confinement of the massif of igneous rocks, that is, the initial carbon was isotopically heavy. Determination of its isotopic composition have the value $\delta C^{13} = -0{,}34$ percent. Probably, isotope fractionation occurred following roughly the same mechanism as in the laboratory experiment with the synthesis of graphite from the gas phase.

Another example can be the sample of graphite from the apatite-natrolite vein of Mount Yukspor in the Khibiny Range, representing an extremely Recent pseudomorphism in aegerite (sample of I. A. Petersil'ye). The isotopic composition of this graphite is characterized by $\delta C^{13} = -1{,}52$ percent. It can be assumed that during the substitution of aegirite heterogeneous fractionation of carbon isotopes occurred, leading to some enrichment of it in C^{12} compared with the heavier carbon of endogenic CO_2, CO, or CH_4.

Graphite with a very unusual isotopic composition δC^{13} = = -4.70 percent was found in sheaflike-fibrous kyanitic shale from Shuururta (Central Keyvy Range). This isotopic composition

is characteristic only of hydrocarbon gases in the upper zone of sedimentary rocks, which can scarcely have a relationship to the formation of the graphite under study. However, present in rocks is much material having an isotopic composition in the range -2.0 to -3.2 percent (bitumens, diffuse carbon, and free methane), /352 which -- considering the additional enrichment in the light isotope in the process of heterogeneous fractionation -- can serve as the initial material for the graphite under consideration.

The isotope effects leading in their way to effects in the system gas - solid can be responsible for the variation in the isotopic composition of graphite during its redeposition. We refer to the possible separation of isotopes during transport reactions. Essentially, the transport reactions consist of a solid interacting in a reversible reaction with some gaseous substance forming mobile products, which after transport to another part of the system with changes in the equilibrium conditions decompose to liberate the initial substance.

A typical transport reaction during which carbon is transported is the Woodward reaction:

From the concept of the mechanism of the heterogeneous fractionation of isotopes, we are correct in anticipating that redeposited graphite will be isotopically lighter than the initial graphite.

In the geochemistry of endogenic carbon, as we have tried to show /26, 29/, there is a clear subdivision of minerals by isotopic composition into two groups: isotopically heavy $\delta C^{13}_{av} = -0.7$ percent (volcanic carbon dioxide, diamonds, carbonates, and juvenile methane) and isotopically light (diffuse carbon and bitumens of igneous rocks); each group is associated with one of the two lines of the evolution of mantle carbon. However, graphites drop out of this scheme, being characterized by a nearly continuous and extremely wide range of δC^{13} values. The possibility of the heterogeneous fractionation of isotopes in the formation of graphite evidently makes possible an explanation of this phenomenon (see Fig. 97). It is not precluded that several other isotopically light forms of carbon of igneous and hydrothermally altered rocks can have their own source of heavy carbon analogous to the carbon in endogenic CO_2, but for their light isotopic composition are indebted to this fractionation mechanism.

It should be stressed that this fractionation mechanism is kinetic in nature and can be manifested in distinction to thermodynamic isotope effects at extremely high temperatures (for example, 1050° C, which occurred in the experiment). Therefore, it can bear special significance for an understanding of isotope fractionation in endogenic processes.

It remains to study the dependence of the direction and magnitude of this effect on temperature, crystallization rate, kind of substrate, concentration, chemical composition of the free phase, and so on, which probably ultimately promises the possibility of employing the heterogeneous fractionation of carbon isotopes for the study of a wide range of geological processes. But at the same time it is specifically the subtle and diverse /353 isotope effects in the formation of graphites that compel caution against overly straightforward conclusions concerning the genesis of graphite from measurements of its isotopic composition.

Gaseous Inclusions in Minerals of Igneous Rocks

Gaseous compounds of carbon associated with magmatic chambers can be of twofold origin. On the one hand, these are the degassing products of the mantle arriving in the lithosphere with volatile constituents of the magmatic melt, and on the other -- gases of metamorphism arising during the thermal decomposition of carbon-containing minerals of the sedimentary complex (see Fig. 97).

The first determinations of the isotopic composition of carbon in gases of hot springs showed that the isotopic composition of CO_2 varies from -0.1 to -1.0 percent, and for CH_4 -- from -1.9 to -2.9 percent. Methane in free gas emanations observed in massifs of igneous rocks has approximately the same isotopic composition /47, 75/.

In conditions of elevated temperatures (300-500° C) in the system CO_2 - CH_4 equilibrium of isotopic exchange is reached quite rapidly. As a consequence, shown by us earlier, in the thermal zone of the earth, regardless of their origin gases acquire -- through secondary exchange -- an isotopic composition determined only by local temperature conditions and by the relative concentrations of CH_4 and CO_2 /29, 116/. Primordially isotopically light methane (formed from organic matter) is here enriched in C^{13}, while juvenile methane, isotopically heavy, is enriched in C^{12} to δC^{13} values determined by the equilibrium with CO_2 (approximately from -2.0 to -2.8 percent), given the condition that CO_2 predominates in the system. If CO_2 is absent, the methane that results from thermal metamorphism of organic matter will contain isotopically lighter carbon (δC^{13} from -2.5 to -3.3 percent), though substantially heavier compared with normal catagenic methane (see Fig. 97).

To study the isotopic composition of endogenic gases unchanged -- as far as possible -- by processes of secondary exchange, together with I. A. Petersil'ye we turned to the analysis of gases in closed pores of igneous rocks and rock-forming minerals. The main object of the investigation was plutons of ultrabasic alkaline igneous rocks of Kola Peninsula (Khibinskiy, Lovozerskiy, Kovdorskiy, and Monchegorskiy). The Khibiny Range, as is known, is the world's largest intrusion of alkaline rocks. It was formed by complexes of nephelinic syenites, granitoid and trachytoid khibinites, ristschorrites (poikilitic nephelinic syenites) and jolite-urtites, lujavrites, and foyaites. The Lovozerskiy massif of alkaline rocks is close to the Khibinskiy in composition and texture. The central part of the Kovdorskiy massif is overlain with olivinites, pyroxenites, and peridotites. Ultrabasic rocks /354 bear magnetite mineralization. Alkaline rocks, developed in the peripheral section, consist of ijolites, melteigites, and ijolite-urtites. It is assumed that alkaline rocks formed from the metasomatic alteration of pyroxenites of the central core under the effect of high-temperature endogenic solutions. The Monchegorskiy massif is formed by ultrabasic and basic rocks -- by peridotites, pyroxenites, and norites.

Gases have been detected in all types of igneous rocks. Especially significant are the content values of gases in alkaline rocks of the Khibiny and Lovozerskiy massifs -- from 12.5 to 82.5 cm^3 per kg of rock /95/. Methane is the predominant constituent (86-93 percent). Also present are ethane, propane, and butane. Unsaturated hydrocarbons have not been found. The concentrations of hydrocarbons gases were established as dependent on the amount of Al_2O_3, that is, essentially on the nepheline content in rock.

On the average rocks of other massifs (Kovdorskiy, African, and Monchegorskiy) contain much less gas. In contrast to the Khibiny and Lovozerskiy massifs, the methane content here is slight (averaging 2.4 percent), and there are traces of heavier hydrocarbons. The main gas constituents are carbon monoxide (averaging 58.3 percent) and hydrogen (averaging 19.8 percent).

Besides gases from igneous rocks of the Kola Peninsula, also analyzed was gas from naujaite (Illimaussak massif, Greenland), and also from rocks of the Kiya-Shaltyrskiy ultrabasic alkaline massif.

Results of isotopic analyses /47/ showed that typical of methane trapped in the pores of igneous rocks is the substantial enrichment in the heavy carbon isotope. The δC^{13} values characterizing the isotopic composition of the carbon in methane from khibinites, ijolite-urtites, foyaites, and naujaite constitute a series from -0.32 to -1.28 percent; these figures lie in the

range characteristic of the mantle degassing products, that is, the carbon compounds associated with the concentrated form of mantle carbon, deriving its origin from the cosmogenic carbon of the carbonaceous chondritic type. We note, by the way, that endogenic carbon may have arrived in the magmatic melt not necessarily in the form of CH_4. It is not precluded that carbon monoxide was primordial. In the presence of hydrogen and as a consequence of the catalytic action of Al_2O_3-rich rocks, CO carbon may have passed into the CH_4 form in a process analogous to the Fischer-Tropsch process. Since in this process the main product of the conversion of carbon monoxide is methane, this latter compound acquired the isotopic composition of the primordial carbon (see Fig. 97).

Somewhat less enriched in the heavy isotope are the free gases from igneous rocks. They were sampled from gaseous inclusions in the prospecting holes of the Kirovskiy Mine (Khibiny Range). Characteristic of these gases are δC^{13} from -1.3 to -1.9 percent. The isotopic composition of the free gases was altered by secondary processes, therefore it differs from the isotopic composition of gas isolated in rock pores, although it remains incomparably heavier than the composition of the gases in sedimentary rocks. /355

Detailed analyses of gases in igneous rocks were continued by V. S. Prokhorov and S. V. Ikorskiy, who studied the isotopic composition of carbon in gases in gaseous inclusions of individual minerals from various pegmatite formations of the Khibiny massif, whose coarse granularity makes it possible to sample a monomineralic fraction. The results of the chemical and isotopic analyses of the gases analyzed are given in Table 79. The isotopic composition of methane carbon varies in the limits from -0.43 to -1.14 percent. Therefore, the isotopic composition of the carbon in gas from gas bubbles in crystals of individual minerals and the gas obtained by crushing rock (contained in enclosed pores) is the same. In both cases, probably, the gas is the same. The total content and chemical composition of the gases, as shown by the analyses of I. A. Petersil'ye and S. V. Ikorskiy, were monitored by the mineralogical composition of rocks. The highest methane concentrations are associated with nepheline and potassic feldspars.

The isotopic composition of methane, as far as we can judge from the data in Table 80, does not depend on the properties of the mineral in which it is encountered. There is also no relationship between the isotopic composition of methane and its content in the gaseous inclusion or the content of other constituents.

TABLE 79. ISOTOPIC COMPOSITION OF CARBON IN METHANE FROM GASEOUS INCLUSIONS IN MINERALS OF IGNEOUS ROCKS (KHIBINY MASSIF)

Rocks	Mineral	Chemical composition, %											δC^{13}, ‰
		CH_4	C_2H_6	C_3H_8	$\frac{i}{n}C_4H_{10}$	$\frac{i}{n}C_5H_{12}$	He	H_2	O_2	N_2	CO	CO_2	
Pegmatite in trachytoid khibinite	Nepheline	77.50	3.744	0.408	$\frac{0.085}{0.105}$	$\frac{0.0172}{0.0057}$	Traces	1.36	3.17	10.94	Not det.	0.00	−0.79
	»	84.25	3.609	0.378	$\frac{0.029}{0.082}$	$\frac{0.0126}{0.0052}$	0.011	2.94	1.66	5.95	0.00	0.00	−0.81
Pegmatite in medium-grained aegiritic, nephelinic syenites	Eudialyte	50.03	11.232	2.115	$\frac{0.229}{0.376}$	$\frac{0.0439}{0.0110}$	0.102	30.08	1.20	4.87	Not det.	0.00	−0.46
	Nepheline	83.88	3.609	0.512	$\frac{0.050}{0.120}$	$\frac{0.0232}{0.0083}$	0.00	1.91	1.63	5.05	»	0.00	−0.43
	Aenigmatite	88.57	1.308	0.124	$\frac{0.008}{0.018}$	$\frac{0.0035}{0.0019}$	0.023	2.89	2.06	6.67	»	Traces	−0.61
Pegmatite in medium-grained nephelinic, aegiritic syenites	Nepheline with aegirite	89.84	2.391	0.226	$\frac{0.021}{0.054}$	$\frac{0.0077}{0.0028}$	0.006	3.705	1.18	4.54	Not det.	0.19	−1.14
	Eudialyte	54.10	8.48	1.610	$\frac{0.166}{0.069}$	$\frac{0.0690}{0.0260}$	0.039	29.30	2.205	7.85	»	Traces	−0.81
Pegmatite in sphenic foyaites	Eucolite	76.84	3.564	0.352	$\frac{0.027}{0.081}$	$\frac{0.0132}{0.0033}$	0.00	3.84	1.40	9.12	Not det.	0.00	−0.53
Pegmatite in ristschorrite	Nepheline	27.24	1.850	0.164	$\frac{0.011}{0.039}$	$\frac{0.0061}{0.0026}$	0.017	4.43	13.47	52.11	Not det.	Not det.	−0.92
Pegmatite in ijolite-urtites	Nepheline	89.42	3.519	0.373	$\frac{0.035}{0.077}$	$\frac{0.0152}{0.0048}$	0.031	3.32	1.63	5.22	0.00	1.46	−0.62

The analyses show (Table 80) that the carbon in CO_2 from gaseous inclusions is markedly enriched in C^{13} compared with the accompanying methane. Obviously, the fractionation occurred with the cooling of the intrusion resulting from the isotopic exchange in the system CO_2 - CH_4. Here, in accordance with the thermodynamic isotope effect of this system, the CO_2 is enriched in C^{13} and CH_4 -- in C^{12}. Since in contrast to the volcanic gases, the CO_2 in gaseous inclusions occupies a subordinate position, only its isotopic composition changed markedly. Methane inherited nearly unchanged the isotopic composition of the initial carbon.

The CO_2 obtained in the Fischer-Tropsch process has a substantially heavy carbon. Possibly, sometimes enrichment in the heavy isotope of carbon dioxide in gaseous inclusions, and also the formation of isotopically heavy carbonates -- observed, for example, by P. Diens [141] (carbonate inclusions and veins 1-2 mm thick in peridotite dikes belonging to the zone of ultrabasic rocks of North America have δC^{13} from +1.2 to +2.48 percnet) -- are caused by processes of this type.

A comparison of the δC^{13} values of endogenic hydrocarbons and crudes and gases of sedimentary rocks shows that methane in sedimentary rocks (δC^{13} from -3.2 to -7.2 percent, with a mean δC^{13} value of -4.2 percent) sharply differs from the methane in igneous rocks in isotopic composition.

TABLE 80. ISOTOPIC COMPOSITION OF CARBON IN CARBON DIOXIDE FROM GASEOUS INCLUSIONS IN MINERALS OF IGNEOUS ROCKS (KHIBINY MASSIF) /358

Mineral	Chemical composition, %										δC^{13}, %	
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	He	H_2	O_2	N_2	CO	CO_2	CO_2	CH_4
Feldspar	89.04	3.003	0.541	—	0.00	0.92	1.22	2.03	0.36	7.68	−0.85	−1.46
Eudialyte	57.79	7.462	0.962	—	0.25	27.75	0.88	3.06	0.78	0.26	+1.06	−0.84

As already noted, the CH_4 existing in conditions of a magmatic melt, of the same isotopic composition as the carbon dioxide (δC^{13} = -0.7 percent) and the carbonaceous matter of the mantle, upon entering the zone of more moderate temperature through exchange with CO_2, begins to be enriched in C^{12} to values established in volcanic gases and emanations of hot springs, that is, to -2.4 percent. The lower the temperature of the medium, the larger the equilibrium constant of isotopic exchange in the system CO_2 - CH_4, the ligher becomes the methane carbon. However, the enrichment of endogenic methane in C^{12} has a limit. When the temperature is lowered to 150° C and below, the rate of isotopic exchange falls to the extent that the equilibrium in the system CO_2 - CH_4 does not set in even during geologic time, which was shown experimentally. Therefore, heavy endogenic methane cannot be enriched

in the light isotope more than δC^{13} values of about -2.5 to -3.0 percent; by this it differs significantly from the isotopic composition of sedimentary rock methane (both diffuse, as well as pool methane).

Thus, a comparison of the isotopic composition of endogenic methane and sedimentary rock methane fully shows that sedimentary rock methane cannot have as its source methane of plutonic origin.

Even more revealing is the difference in gases of sedimentary and igneous rocks as to the nature of the distribution of carbon isotopes in the system CH_4—C_2H_6—C_3H_8.

Individual Hydrocarbons (Methane, Ethane, and Propane)

The isotopic analysis of heavy homologs of methane contained in gaseous inclusions in igneous rocks is fraught with major difficulties in view of their negligible amounts.

In the gas isolated from urtite (Table 81) ethane has δC^{13} = -2.45 percent, and propane -- $\delta C^{13} = -2{,}60$ percent, that is, the isotopic compositions of these hydrocarbons are found to be in inversional relationships compared with the hydrocarbons of oil-gas pools. Methane in this sample was not analyzed, but in similar samples it was characterized by $\delta C^{13} = -0{,}8$ percent. Ethane isolated from eudialyte in two samples yielded /359 somewhat different δC^{13} values (-1.42 and -1.00 percent), but in both cases corresponding to isotopically heavy carbon. Methane from the same sample contained even heavier carbon ($\delta C^{13} = -0{,}79$ percent), and propane was not analyzed. All three hydrocarbons were analyzed in the trachytoid khibinite. Methane most highly enriched in the heavy carbon isotope (δC^{13} = -0.32 percent) and ethane most highly enriched in the heavy isotope ($\delta C^{13} = -0{,}91$ percent) were established in this sample. It is easy to see that the nature of the distribution of carbon isotopes in the individual constituents of the gases analyzed from the igneous rocks is wholly distinct from their distribution in any of the sedimentary rock gases studied (Fig. 100).

This feature was used for the determination of the genesis of hydrocarbon gas in free emanations observed in mine workings of the Sopcha Mine (Monchegorskiy massif). The gas was sampled by I. A. Petersil'ye at the heads of wells drilled from drifts with markers of minus 150-191 m (the surface marker was approximately +300 m). Water and gas entered from a depth of approximately -300 m from pyroxenite-perioditites. As was clear from Table 81, the isotopic composition of methane, ethane, and propane in this gas was found to be in relationships characteristic

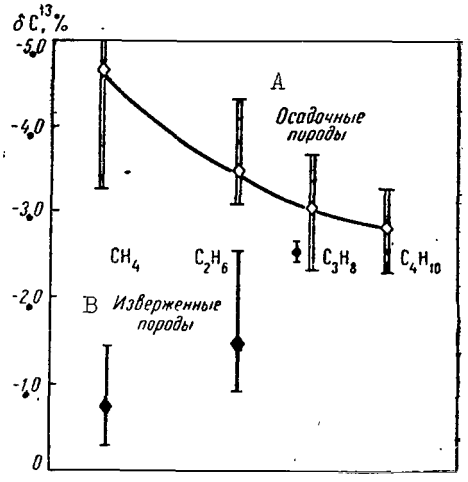

Fig. 100. Comparison of the nature of the distribution of carbon isotopes in gaseous hydrocarbons of sedimentary and igneous rocks
KEY:-A. Sedimentary rocks
B. Igneous rocks

of gases in sedimentary rocks formed in moderate metamorphism of organic matter and distinct from the isotopic composition of the corresponding constituents of gaseous inclusions in the minerals of igneous rocks.

The increase in the concentration of C^{13} in the series $CH_4—C_2H_6—C_3H_8$ characteristic of sedimentary rock gases is associated, as shown above, with the kinetic and intramolecular isotope effect manifested in the decomposition of a complex organic compound. The reverse character of the distribution of isotopes and individual hydrocarbons from the gaseous inclusions indicates that here there is rather the synthesis of high-molecular constituents from simple compounds, for example, with the participation of free radicals: $CH_4 + CH_3^{\cdot} \rightarrow C_2H_6 + H^{\cdot}$; $C_2H_6 + CH_3^{\cdot} \rightarrow C_3H_8 + H^{\cdot}$. If $CH_3^{\cdot}$ was formed via the scheme $CH_4 \rightarrow CH_3^{\cdot} + H^{\cdot}$, then the cleavage of hydrogen gives the kinetic isotope effect for carbon, which as $T \rightarrow \infty$ (virtually for 600-800° K) can be estimated with a good approximation by the ratio of the reduced masses, that is, it is approximately 1.002. This corresponds to enrichment of the $CH_3^{\cdot}$ carbon in the light isotope relative to the methane carbon by 0.2 percent.

The thermodynamic isotope effect has a marked value. Table 82 lists the β-factors of $CH_3^{\cdot}$ for different temperatures calculated by the method of isotopic bond numbers. Their comparison with the β-factors of CH_4 shows that at 1000° K enrichment of the methyl radical carbon in the light isotope is approximately 0.5 percent. At lower temperatures the isotope effect is enhanced.

Thus, the formation of ethane and propane from methane in reactions involving the participation of free radicals in principle can explain the enrichment of high-molecular hydrocarbons in the light isotope, if one starts from the primacy of isotopically heavy methane or carbon dioxide, that is, the primacy of the isotopically heavy carbon of the mantle of the carbonaceous chondrite type.

TABLE 81. ISOTOPIC COMPOSITION OF CARBON IN INDIVIDUAL HYDROCARBONS IN IGNEOUS ROCK GASES

Mineral	Chemical Composition, %											δC^{13}, %		
	CH_4	C_2H_6	C_3H_8	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	He	H_2	O_2	N_2	CO_2	CO	CH_4	C_2H_6	C_3H_8
Uritite*	61.64	1.68	0.147	0.014	—	0.12	2.75	—	—	Traces	—	−1.28	−2.45	−2.60
Khibinite*	76.64	3.16	0.253	0.100	0.019	0.005	5.60	0.8	8.0	0.00	0.05	−0.32	−0.91	−2.57
Eudialyte**	45.7	9.00	2.28	0.370	0.180	—	34.4	2.1	10.5	Absent	0.5	−0.79	−1.42	—
Periodotite***	65.55	0.57	0.031	0.001	0.001	2.31	0.15	0.26	31.0	Absent	0.5	−4.80	−1.00 −3.61	— −2.62

* Gas in enclosed pores of rocks (Khibiny massif)
** Gaseous inclusions in mineral (Khibiny massif)
*** Free gas emanation in peridotites (Monchegorskiy massif)

TABLE 82. THERMODYNAMIC ISOTOPE FACTORS OF CH_4 and CH_3^* AND VALUES OF ISOTOPIC SHIFTS IN THE SYSTEM

T, K	300	400	600	800	1000	1200	1300	1500
CH_4	1.1136	1.0765	1.0421	1.0267	1.0184	1.0134	1.0115	1.0089
CH_3^*	1.0855	1.0573	1.315	1.0198	1.0138	1.0102	1.0087	1.0066
ΔC^{13}, %	−2.81	−1.92	−1.05	−0.69	−0.46	−0.32	−0.28	−0.23

$\Delta C^{13} = 10^2 \ln \beta_{CH_3^*}/\beta_{CH_4}$

Bitumenoids of Igneous Rocks and Their Fractions

Polymeric carbon compounds of the bitumen type are widely distributed in igneous rocks, though their concentrations usually do not exceed the limits of thousandths of a percent. In the journal literature periodically there are reports on finds and results of investigations of such formations.

We studied a fairly broad series of bitumens from igneous and metamorphic rocks (see Fig. 96). More detailed information is to be found in the paper [48]. The range of variations in the isotopic composition of carbon of the bitumens analyzed is characterized by δC^{13} from -2.67 to -3.23 percent, with a mean δC^{13} = -2.95 percent. Thus, bitumens of igneous rocks belong to the group of carbon compounds relatively enriched in C^{12}.

The mean isotopic composition of carbon of bitumens in different intrusions is quite close: Lovozerskiy massif -- δC^{13}_{av} = -2.96 percent, Khibinskiy massif -- δC^{13}_{av} = -2.91 percent, Kovdorskiy massif -- δC^{13}_{av} = - 2.97 percent, Sredne-tatarskiy massif -- δC^{13}_{av} = -2.94 percent, Kiya-Shaltyrskiy massif -- δC^{13}_{av} = = -2.95 percent, and so on.

Concerning dispersed bitumens, the hypothesis was raised that their formation is associated with the processes of homogenization of diffuse carbon in igneous rocks. In this case, the isotopic lightness of the bitumens is accounted for by their belonging to the second line of the evolution of mantle carbon, deriving its origin from the diffuse form of cosmic (meteoritic) carbon [26].

Isotope effects observed in the Fischer-Tropsch process in principle allow us to assume as possible the formation of isotopically light bitumens of igneous rocks from isotopically heavy initial carbon present as CH_4 or CO. It stands to reason that in this case, as well as in the synthesis of ethane and propane, free-radical polymerization took place.

Table 83 gives the results of an analysis of different forms of carbon present in the same sample of igneous rock. Trachytoid khibinite was analyzed -- the characteristic rock of the Khibiny intrusive massif, which is a variety of nephelinic syenite of trachytoidal texture, usually containing eudialyte.

Included in the composition of the gas isolated from the rock is methane, as the predominant constituent. As in other igneous rocks of the Khibiny massif, methane carbon is isotopically heavy. The distribution of carbon isotopes in methane, ethane,

TABLE 83. ISOTOPIC COMPOSITION (δC^{13}, PERCENT) OF VARIOUS FORMS OF CARBON IN TRACHYTOID KHIBINITE (KHIBINY MASSIF AND KOLA PENINSULA)

Chloroform-extracted bitumenoid	Residual carbon after extraction of bitumenoid	Residual carbon after calcining at 600° C	Gas released in calcining	Bitumenoid fraction			
				solid paraffin	methane-naphthenic	aromatic	benzene-tars
-2.70	-3.41	-1.96	-2.57	-2.87	-2.80	-2.63	-2.70

Bitumenoid fraction (continued)		Gas extracted from rock		
alcoholic-benzene tars	asphaltenes	CH_4	C_2H_6	C_3H_8
-2.70	-2.74	-0.32	-0.91	-2.57

and propane forms an invertional pattern if we compare it with the distribution pattern of isotopes in the corresponding constituents of crude oils and gases from sedimentary strata. At the same time, the ratio of the isotopic composition of carbon in hydrocarbon fractions of the bitumenoid analyzed resembles the ratio of the isotopic composition of carbon in the corresponding classes of petroleum hydrocarbons. Most strongly enriched in C^{12} are the solid paraffins ($\delta C^{13} = -2.87$ percent). The methane-naphthene fraction ($\delta C^{13} = -2.80$ percent) is isotopically lighter than the aromatic ($\delta C^{13} = -2.63$ percent). Asphaltine-tarry constituents have an intermediate isotopic composition, just as in the crudes. The carbon isotope distribution observed in crudes, as was shown above, to a large extent is a consequence of isotopic equilibrium in the initial biological systems.

The similarity noted here between the isotopic composition of petroleum fractions and bitumenoid extracted from igneous rock must signify that in the process of abiogenic synthesis there was also present the equilibrium isotopic exchange of carbon. The distribution observed can be caused by thermodynamic isotope effects if the formation of the bitumenoid took place at temperatures not above 500° C. But whether at these or lower temperatures, the attainment of isotopic equilibrium in high-molecular (abiogenic) systems appears problematical.

Analysis of the naphthenic fractions separately would be extremely important. In any abiogenic systems the synthesized naphthenic and aromatic hydrocarbons must have approximately the same isotopic composition (in correspondence with their β-factors). This is actually observed, for example, in the products of the thermocatalytic synthesis of hydrocarbons (see Chapter Four). In crude oils, naphthenic hydrocarbons are isotopically lighter than aromatic.

Chloroform-extracted bitumenoid proved to be isotopically not the lightest form in the rock, since residual carbon after extraction had $\delta C^{13} = -3.41$ percent compared with $\delta C^{13} = -2.71$ percent and $\delta C^{13} = -2.68$ percent established for the bitumenoids. At the same time the carbon remaining in the rock after the distillation of all fractions volatile up to 600° C is somewhat depleted in C^{12} ($\delta C^{13} = -1.93$ and -1.99 percent).

Hydrothermal Formations

Bitumens associated with hydrothermal mineralization were analyzed in several mercury deposits of the Northwest and Central Caucasus, and also within the Tamvatneyskiy massif in Eastern Siberia.

In the deposits of the Northwest Caucasus, ore is found in sedimentary strata of the Lower Cretaceous as a rule in tectonic breccias -- in those areas where major upheavals intersect the most elevated sections by anticlines (the deposits Pereval'noye, Belokamennoye, and so on). The Upper Jurassic strata underlying the ore-bearing horizon are represented by bituminous limestones, marls, and shales. From the description of A. I. Germanov and L. A. Bannikova, characteristic of the zone of sulfide mineralization directly adjoining the fault is a solid bitumen of the idrialite type, whose deposition occurred in the post-mineralization stage. In a zone that is external with respect to the sulfide zone, numerous veins of calcite are developed, with which a material of the kerite type is associated. Kerites are found both along the periphery of the calcite zone as well as at the boundary with the sulfide zone, where they are intersected by veins of cinnobar, which permits classifying them with the presulfide formations. Kerite has a quite stable isotopic composition, characterized by the mean value $\delta C^{13} = -2{,}32$ percent (from -2.17 to -2.37 percent), that is, the carbon of hydrothermal kerites is isotopically heavier than the carbon of diffused bitumens of unaltered sedimentary rocks for which $\delta C^{13} = -2{,}8$ percent is typical. The carbon of idrialite from ore-bearing breccia is even more enriched in the heavy isotope ($\delta C^{13} = -2{,}06$ percent). /364

Most likely, hydrothermal bitumen is the product of the redeposition of bitumens from sedimentary rocks mobilized by hot ascending solutions. Measurement of the isotopic composition of organic matter from ore-intervening clays gave $\delta C^{13} = -2{,}55$ percent. Possibly, during redeposition isotope fractionation occurred similar to what was observed in the experiments with the sublimation of bitumens (see above). As a result, hydrothermal bitumen, which is the most mobile fraction of the initial sedimentary bitumen, came to be somewhat enriched in the heavy carbon isotope.

The isotopic composition of carbon in calcite films found in association with bitumens bears no traces of the influence of the isotopically lighter carbon of the bitumen. Calcite veins have an isotopic composition from + 0.19 to -0.23 percent (δC^{13}_{av} = +0.04 percent), that is, virtually coinciding with the isotopic composition of the carbonate material of ore-intervening sedimentary strata, which evidently also served as the starting material for the hydrothermal calcite. Hence it can be concluded that the formation of the hydrothermal bitumen and the corresponding changes in the isotopic composition of its carbon were completed by the time the bitumen was deposited.

The distribution of carbon forms in the case of mercury mineralization in the El'brus polymetallic deposit, examined by

us together with A. I. Germanov and O.V. Nikolayeva, is of a different kind. In distinction to the mercury deposits of the Northwest Caucasus confined to sedimentary rocks, here the ore bodies lie in intrusions (quartz porphyries) and crystalline shales. Here any direct contact with carbonate and bitumenous rocks, as in the North Caucasus deposits, is absent. Along the primary tectonic disturbance of the thrust type ("sloping zone") in the overhanging margin of which lie the ore veins, a rich graphitic mineralization is developed, but there are no bitumens, and a graphitelike material acts as a cement in the fracturing zone. The isotopic composition of the graphite varies markedly -- from -0.73 to -3.05 percent. Mostly, samples whose isotopic composition is -1.9 to -2.0 percent are found. Hydrothermal calcite accompanying the sulfides is enriched in C^{13} on the average by 0.2 percent, and in some cases by 0.5-0.6 percent more than typical sedimentary carbonates, and thus is isotopically heavier than hydrothermal calcites from mercury deposits of the Northwest Caucasus. Along the Tsentral'nyy section the calcite has δC^{13} from + 0.18 to + 0.65 percent, along the section Khudes -- -- from + 0.08 to + 0.16 percent, and along the section Daut -- -- from + 0.29 to + 0.66 percent. Here the isotopically heaviest calcite is associated with the isotopically heavy graphite (δC^{13} from -0.73 to -1.13 percent). /365

Enrichment of the hydrothermal calcites in the heavy isotope is not a rarity /29, 52/. The simplest explanation, and probably the one corresponding to the most common case, is the inversion of the thermodynamic isotope effect in the system $CO_2 \rightleftarrows CO_3^=$. At low temperatures the exchange reaction is shifted toward the side of C^{13} in the carbonate, but at T $>130^{\circ}$ C the heavy isotope begins to be concentrated in carbon dioxide. The inversional effect reaches a maximum at 425° C. Thus, the carbon dioxide entering into solution when carbonate rocks are leached by high-temperature water at equilibrium is enriched 0.2-0.4 percent in C^{13}. When due to this carbon dioxide calcite is deposited from the cooled solution in the unloading zones, the separation in the exchange system is now directed toward the side of depletion of carbon dioxide in C^{13}. Thus, the isotope effects are superimposed and the hydrothermal calcite formed can be considerably enriched in the heavy isotope (see Fig. 97). It is only important that in the interval between the high-temperature leaching and low-temperature deposition of calcite, the hydrothermal solution be isolated from the carbonate rocks. Continuous exchange with carbonates will lead to the permanent alteration of the isotopic composition of the carbon dioxide in the solution with change in conditions. Then the calcite will not differ in isotopic composition from the initial carbonate. Obviously, corresponding to the latter case are the conditions of the formation of the calcite mineralization of the Northern Caucasus, while the geologic conditions of the El'brus deposit may have wholly been responsible for the inversional enrichment of calcite in the heavy isotope.

Under otherwise equal conditions, the heavy isotope enrichment of hydrothermal calcite associated with igneous (noncarbonate) rocks must have been greater, the higher the temperature at which the primary mobilization of the carbonate carbon by the hydrothermal solution took place, and the lower its deposition temperature. In the section Daut of the El'brus deposit where calcite is associated with barite and evidently corresponds to the lower-temperature stage (80-100° C) of the hydrothermal process, the isotopic composition of calcite is characterized by the highest δC^{13} values (averaging about + 0.60 percent).

By comparing the two types of the mercury deposits, one of which is confined to the sedimentary strata, and the other -- to the igneous rocks, we find a characteristic difference in the form of occurrence and the isotopic composition of carbon, In the first case, with the presence of the carbonate-bituminous sedimentary strata, in hydrothermal formations are found bitumen and calcite whose isotopic composition coincides with that of the sedimentary carbonates. In the second case, when the hydrothermal process developed chiefly in rocks free of primary /366
carbonate content and bituminosity, graphitic mineralization is observed and calcite enriched in the heavy isotope is deposited. The strong influence that the material of sedimentary rocks has on the nature of the hydrothermal process affords grounds for assuming that the appearance of bitumens in hydrothermal formations of the North Caucasus deposits is associated with processes of the hydrothermal redeposition of material borrowed from the bituminous carbonate rocks underlying the ore-intervening strata.

But obviously, hydrothermal bitumens do not always originate from the bitumens of sedimentary rocks. The isotopic composition of carbon was studied in samples presented by Yu. A. Kolesnikov for a number of hydrothermal formations of the Tamvatneyskiy massif of peridotites and the Tamvatneyskiy mercury deposit of the listvenite type. The massif lies in the jointing zone of the structures of the Koryakskiy highlands and the Anadyrskaya Depression. On the northwest it is in contact with sedimentary rocks of Mesozoic age. The contact zone is complicated by a series of faults controlling, in particular, the mercury mineralization. Widely developed in blocks of peridotites are stocks and dikes of pegmatoid gabbro. Along the contacts with the gabbro, as well as in the ore-controlling faults the peridotites are serpentinized, and there appears the highly characteristic variety of the so-called black serpentinites. The black color is due to the presence of a finely dispersed dust (particle size less than 10^{-4} mm), which in the opinion of geologists (P. V. Babkin and Yu. A. Kolesnikov) is some form of carbon, possibly associated with iron. Black serpentinite has an unusually low magnetic

susceptibility (540 SGS units as against 7180 SGS units for normal serpentinite, from the data of Yu. A. Kolesnikov), that is, the iron of silicate during serpentinization was segregated in it not as the magnetite, as is usually the case.

Processes of listvenitization and silicicification of serpentinites through their subsequent hydrothermal treatment leads to the substitution of the "dust" with finely dispersed marcasite-pyrite. At the same time bitumens appeared, whose formation supposedly is associated with the mobilization of the diffuse carbon of "black serpentinites." Bitumen containing sulfides (cinnobar) are found as inclusions in listvenites and quartzites.

In rocks of sedimentary strata bounding the peridotite massif on the north, the presence of hydrocarbon substances (anthraxolites) is noted in a zone encompassed by an intensive idle thermal process. The concentration of carbon-containing substances is very low in the unaltered rocks of this same strata.

Measurement of the isotopic composition of diffuse carbon of "black serpentinite" gave the value $\delta C^{13} = -1.43$ percent (Table 84). It is in the range of δC^{13} values that are characteristic of graphites formed with a heterogeneous isotope effect from isotopically heavy carbon dioxide. Endogenic carbon dioxide participated in the processes of serpentinization and listvenitization. Analysis of the sample of aragonite from gryphon in the serpentinization zone deep inthe peridotite massif gave the value δC^{13} = -0.01 percent. Carbonate travertine (magnesite-dolomite containing chalcedon) in the same section has δC^{13} = = + 0.71 percent. Enrichment in the heavy carbon isotope is characteristic of the travertines. We observed this earlier in the example of Kamchatka and Caucasus travertines, where samples with δC^{13} = + 1.46 percent are found. Thus, in hydrothermally altered peridotites forms of carbon are found that have as their source endogenic carbon dioxide ($\delta C^{13} = -0.7$ percent) and differ from it in isotopic composition by a value that is anticipated and explainable by known isotope effects. /367

Bitumenoids contained in quartz veins of listvenitized serpentinite are characterized by a different isotopic composition -- from -1.72 to -2.57 percent. If they had been formed through the hydrogenation of diffused carbon of serpentinites, which in general is not contradicted by the isotopic analysis of bitumenoids, it must be assumed that there was an imposed process of isotope fractionation leading to the depletion of the bitumen carbon in C^{13} and to a wider series of variations in δC^{13}. This process may have been the secondary sublimation /368

TABLE 84. ISOTOPIC COMPOSITION OF CARBON IN HYDROTHERMAL FORMATIONS OF THE TAMVATNEYSKIY PERIDOTITE MASSIF AND THE TAMVATNEYSKIY MERCURY DEPOSIT

Sample description	δC^{13} ‰
"Black serpentinite"	-1.43
Bitumen in quartz vein from listvenitized serpentinite deep in the peridotite massif	-1.96
Bitumen in drusoid quartz from quartzites deep in massifs of peridotites (approximately from the same area as the preceding sample)	-2.43
Bitumen in quartz from listvenitized serpentinite in the zone of contact hydrothermal alterations	-2.57
Bitumen in listvenitite type of mercury ore manifestation	-2.57
Carbonaceous matter in hydrothermally altered peridotite	-1.72
Anthraxolite from zone of maximum concentration of bitumens in altered sedimentary rocks at contact with peridotote (listvenites)	-2.55
Anthraxolite from contact zone of hydrothermally altered sedimentary rocks	-2.54
Carbonaceous matter of the anthraxolite type, but without lustre (from the same area as the preceding sample)	-2.45
Anthraxolite in quartz-chalcedon veins from ore manifestation in the Tamvatneyskaya suite (sand-shale strata) along the west of the peridotite massif	-2.52
Aragonite from gryphon in the zone of serpentinization deep in the peridotite massif	-0.01
Travertine (magnesite and dolomite containing chalcedon) in the zone of hydrothermal alteration of peridotites	+0.71

of bitumens, during which time the isotopic separation that we observed in the laboratory sublimation of bitumen may have possibly occurred. N. T. Sokolova et al. [100] described the clarifying of black shales close to a hydrothermal uranium mineralization that was similar to this case. The black color was caused by the presence of disseminated flakes of graphite (0.01 mm), which was identified by their reflectivity. We note that in black serpentinite the size of flakes is two orders of magnitude smaller, therefore it is not possible to estimate the reflectivity. The authors of this study assume that the clarifying occurred through the oxidation of the graphite to CO and CO_2, which then entered the hydrothermal solution.

If something similar is assumed in our case, then it would be logical to relate the formation of bitumens at a later stage with the Fischer-Tropsch reactions. Carbonaceous polymeric material through fractionation in the Fischer-Tropsch is enriched in C^{12} relative to the initial CO. This may have accounted for the difference between the isotopic composition of the carbon in black serpentinites and the isotopic composition of bitumen carbon. It should be considered that the oxidation of graphite, as was shown in the experiments of A. P. Vinogradov and coworkers [19], takes place in certain cases with the fractionation of isotopes and can lead to the enrichment in C^{12} of gaseous products of oxidation.

Principles of the Identification of Biogenic and Abiogenic Organic Compounds

From the foregoing it is clear that bitumens extracted from various magmatic rocks and hydrothermal formations as a whole are isotopically light. Characteristic of these bitumens are δC^{13} values from -2.0 to -3.0 percent.

Approximately the same range of δC^{13} values is reported by other investigations studying hydrothermal bituminous substances. J. Hoefs and M. Schidlowski [169] established δC^{13} values from -2.24 to -3.28 percent for seven samples of tucholite from gold-bearing conglomerates of the Witwatersrand (South Africa). Analysis of alcoholic-benzene bitumenoid from a quartz vein in hydrothermally altered Precambrian rocks of Southwest Africa, conducted by K. Kvenvolden and E. Roedder [183], gave in two determinations δC^{13} = -1.98 percent and δC^{13} = -2.01 percent. R. V. Zezin et al. [58], on investigating several asphaltite minerals, obtained C^{13} values from -1.08 to -3.55 percent.

On examining the data on the isotopic composition of carbon of hydrothermal bitumens when compared with the bitumens and crude oils from sedimentary rocks, it can be concluded that on the average, either case has closely similar δC^{13} values. Accordingly, the question of the nature of the initial matter for the hydrothermal bitumens -- biogenic or endogenic -- cannot be easily resolved on the basis of analyzing only total carbon, since there are biological and nonbiological mechanisms of the formation of carbon of similar isotopic composition, just as there are organic and inorganic compounds that in terms of their isotopic composition could be regarded as precursors of hydrothermal bitumens.

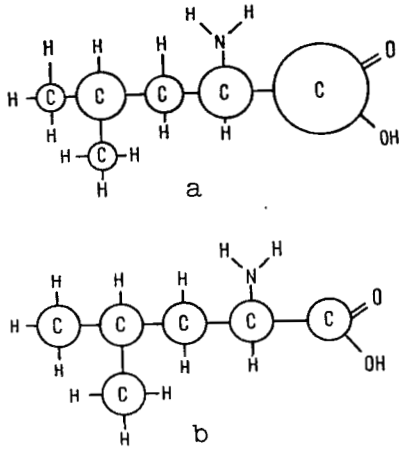

Fig. 101. Example of intramolecular distribution of carbon isotopes in biogenic (a) and abiogenic (b) organic compounds (molecule of the aminoacid leucine)

Thus, deterinations and comparison of mean isotopic compositions of petroleum, organic matter, or bitumens of igenous rocks to which studies have thus far been confined do not permit unambiguous conclusions to be drawn.

New prospects are opened up in this sense by the use of of the phenomenon of intramolecular isotopic nonuniformity of biogenic compounds. Fig. 101 shows the distribution of carbon isotopes in an aminoacid. In the case of the biological synthesis of the aminoacid, the carbon isotopes are distributed nonuniformly in accordance with the intramolecular thermodynamic isotope factors (β_i-factors). In other words, the isotopic composition of the carbon occupying different positions in the aminoacid differs. This is illustrated by the difference in the size of the circles whose diameters are proportional to the β_i-factors of the carbon atoms.

Exactly the same aminoacid, not differing at all chemically from the first aminoacid, but synthesized abiogenically, for example, from mixtures of NH_3, CH_4, H_2O, and so on, will have -- in the light of the concepts we have developed in this book -- an entirely different intramolecular distribution of isotopes that will prove to be practically uniform, or in any case, if we bear in mind the possibility of the abiogenic thermodynamic isotope effects of the first kind (see Chapter Two), the isotopic nonuniformity will be much less than in the very same biogenic aminoacid.

If in a suitable fashion we decompose this aminoacid, then from the value of the isotopic shifts observed in the fragments formed we can establish the origin of this compound -- biological or nonbiological. Here not only the chemical, but also the mean isotopic composition (averaged circle size) of either aminoacid can be the same. Only the intramolecular distribution is decisive. Chapter Two deals with this situation more rigorously.

The problem of identifying the nature of organic compounds has definite significance in oil-gas geology. For a long time there has been under discussion the so-called inorganic origin of petroleum. Today owing to the large number of new data, this problem is becoming less acute. But if extra proof were to be needed, then as one of the most convincing we could bring in the isotopic nonuniformity of petroleum hydrocarbons -- the direct evidence of their biological origin. This isotopic nonuniformity is established by direct measurements of the isotopic composition of various structural groups of petroleum hydrocarbons. From Fig. 51 presented in Chapter Four it is clear to what extent the experimental and calculated values of the isotopic shifts in petroleum aromatic hydrocarbons with different structures coincide.

But today even more urgent is the problem of the origin of organic compounds encountered in situations when clear indications of their possible biological history are altogether lacking. These organic compounds are of singular interest from the standpoint of exobiology (a new direction examining the possibility that extraterrestrial forms of life exist) and from the standpoint of explaining the conditions of the origin of life on Earth. The question is how far can the increasing complexity of organic compounds be advanced abiogenically and, therefore, where is the minimal degree of organization based on which a demarcation line can be drawn between the living and the nonliving.

Quite complicated organic compounds have been found at present in numerous igneous rocks, and also in meteorites, especially in one of the varieties of stony meteorites -- carbonaceous chondrites, whose special role in the formation of the matter of the Earth was discussed by us at the beginning of this chapter. But to regard them as evidence of the abiogenic synthesis of organic compounds would necessitate proving that they are abiogenic.

Usually three approaches are used: measurement of isotopic composition, analysis of optical activity, and ascertaining the typomorphic structures and compounds.

Measurement of the isotopic composition of a compound as a whole, it must be admitted here, yields nothing. We have talke talked about the reasons for this earlier. Optical activity is a strong indicator of organic compounds, but far from all compounds of biological origin are optically active. A highly promising approach, just as in the investigation of crude oils, is the constituent-by-constituent analysis of the most highly individualized possible fractions and individual compounds.

Active attempts of this kind in the analytical-chemical sense, but without the measurement of the isotopic composition, have been recently undertaken by American workers. G. Gibbs [158], for example, analyzed organic matter extracted from chrysotile asbestos of the serpentinite zone of Quebec, which proved to be represented to a large extent by normal C_{16}-C_{26} alkanes. K. Kvenvolden and E. Roedder [183], in studying the composition of inclusions in quartz crystals from calcite veins -- in the Precambrian rocks of Southwest Africa -- found that the high-temperature constituents of the inclusions consist mainly of C_{10} - C_{33} n-alkanes. In addition, isoprenoid compounds were found: phytane, pristane, 2,6,10-trimethylpentadecane, 2,6,10-trimethyltetradecane, 2,6,10-trimethylundecane, and 2,6-dimethylnonane. However, the typomorphicity of the normal alkanes and even the isoprenoids, until recently regarded as a full-fledged indicator of the biological origin of an organic compound, was placed in doubt due to new experiments in their synthesis [225].

Accordingly, isotopic investigations based on fundamental differences in intramolecular distribution in biogenic and abiogenic organic compounds can be especially useful.

Among other things, isotopic analysis of the carbon in isoprenoids, probably even without the procedure of the decomposition of the molecules, could permit a differentiation to be made between biogenic and synthesized isoprenoids. Actually, the values of the β-factor formed by the sum of the isotopic bond numbers of a segment of the isoprenoid chain and the corresponding segment of the normal chain of hydrocarbon atoms are virtually the same.

This means that in organic matter the isotopic composition of the carbon in corresponding structures, for example, the phytoles, and the radicals of saturated fatty acids must be the same. Therefore, isoprenoid hydrocarbons, whose structure is most likely inherited from the structure of phytole, must in addition to normal alkanes be classed with the isotopically lightest compounds in crude oils, while other hydrocarbons with isostructures formed during secondary reactions are noticeably enriched in the heavy carbon isotope (see Chapter Four). Hence we clearly see the principle of identification: biogenic isoprenoids in crude oils must be isotopically lighter than any other isostructural hydrocarbons. As for possible abiogenic isoprenoids, there are no grounds to expect that they will differ in isotopic composition from other branched hydrocarbon with similar molecular weight.

This discussion outlines only one of the possible approaches based on analyzing intramolecular isotope effects that -- in our view -- open up new vistas in understanding the genesis of matter, in particular, in determining biogenic and abiogenic forms of carbon.

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